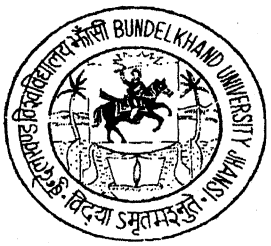
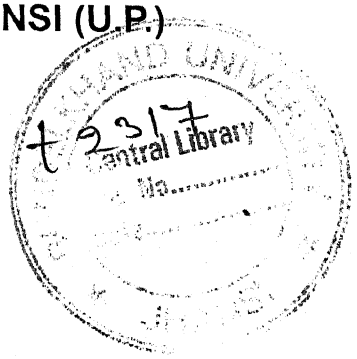
# THE SYNTHESIS AND STRUCTURAL STUDIES OF COORDINATION COMPOUNDS OF CHROMIUM (I) WITH SUBSTITUTED URACIL AND IMIDAZOLES

## Thesis

SUBMITTED TO
BUNDELKHAND UNIVERSITY JHANSI (U.P.)




FOR THE DEGREE OF

## DOCTOR OF PHILOSOPHY
## IN
## CHEMISTRY

By

**VIJAYA DUBEY**

UNDER THE SUPERVISION OF

**DR. AWADHESH CHANDRA NIGAM**

DEPARTMENT OF POST-GRADUATE STUDIES AND RESEARCH IN CHEMISTRY

ATARRA P.G. COLLEGE, ATARRA (BANDA)

**2006**

*Dr. AWADHESH CHANDRA NIGAM*
Principal
Ex–Member, Executive Council
Member, Academic Council
Member, Faculty of Science
Convenor, Research Degree Committee
Convenor, Board of Studies in Chemistry
Bundelkhand University, Jhansi
**ATARRA–POST GRADUATE COLLEGE**
**ATARRA–210201, U.P., INDIA**

**डॉ0 अवधेश चन्द्र निगम**
प्राचार्य,
पू0 सदस्य–कार्यपरिषद
सदस्य–विद्यापरिषद एवं विज्ञान संकाय
संयोजक शोध समिति एवं पाठ्यक्रम समिति
बुन्देलखण्ड वि.वि., झाँसी
**अतर्रा पोस्ट ग्रेजुएट कालेज,**
**अतर्रा 210201, उ0प्र0, भारत**

☎ *05191–211609*
*9450170885*

# ***CERTIFICATE***

This is certify that ***Vijaya Dubey*** Research Scholar in the Department of Chemistry, Atarra Post .Graduate College, Atarra (Banda) has worked for the required period under my supervision for the degree of ***Doctor of Philosophy in Chemistry*** on the topic, ***"The Synthesis and structural studies of coordination compounds of chromium (I) with substituted Uracil and Imidazoles"***. The work reported in this thesis embodies the work of candidate herself.

Dated : 30 Aug. 2006

***[ Dr. A. C. Nigam ]***
Research Supervisor

# ACKNOWLEDGEMENTS

I welcome this opportunity to express my deep sense of gratitude and indebtness to my research supervisor **Dr. A.C. Nigam,** *Principal, Atarra P.G. College, Atarra (Banda)* for suggesting an interesting problem, sagacious guidance, keen interest and discussions, which provided the continuous impetus for the completion of the research work.

My sincere thanks are due to **Sri. Karan Singh,** *President of managing committee Atarra P.G. College Atarra (Banda)* for his constant encouragement and providing necessary facilities.

My Sincere thanks are due to **Dr. D.K. Dwivedi,** Head dept. of chemistry **Dr. P. K. Saxena** and **Dr. S.P. Pandey** for their encouragement, help and affection shown during my research.

I shall be failing in my duty if I do not express my sincere thanks to **Dr. D. C. Gupta**, *Reader, department of chemistry, Atarra P.G. College Atarra (Banda)* for constant encouragement and providing necessary facilities to carry out this work.

I would like to express my sincere thanks to **Dr. R.C. Maurya,** *Reader department of P.G. Studies and Research in Chemistry* and **Dr. M.R. Maurya**, *department of Chemistry*, I.I.T. Roorakee for valuable suggestions.

I would like to express my sincere thanks to **Dr. K. P. Madhusudanan**, *Scientist 'G' and Head SAIF, CDRI, Lucknow*, for providing the facilities for the analysis and recording the spectra of compounds.

I would like to express my thanks to **Mr. Praveen Kumar Mishra,** *Department of Chemistry, Sacred Heart Degree College,*

*Sitapur, U.P.* for his valuable suggestions and providing literature during the course of my research work.

I would like to express my thanks to **Anshu Nigam & Mr. Alakh Narayan Singh**, research scholar *Department of Chemistry, Atarra P.G. College, Atarra (Banda) U.P.* for his valuable suggestions and discussions during my research work.

My Sincere thanks are also due to my father in law **Shri Mishri Lal Dubey** help and affection shown during my research.

My work would never be completed with out the kind blessing and whole hearted support of my husband **Shri Abhay Dubey** *Development Officer, LIC.*

I shall be failing to my duty if I do not recognize my **baby daughter** and **son** who's charming and heart stealing smile has been a source of motivation for me to complete the work.

I also acknowledge my father **Shri M.P. Tripathi** and my brother **S.N. Tripathi,** Sr. Engineer for their possible assistance and encouragement and help affection shown during my research.

In the last I am very thankful to **Mr. Pankaj Kumar Singh & Nishish Shrivastava** *Shri Tulsi Type Centre & Computer's, Atarra (Banda) & NKS Computers, opp. SBI Fatehpur* for the neat and clean typing of my thesis.

Date: 29 Aug. 2006

[ **VIJAYA DUBEY** ]

*Research Scholar*
Department of chemistry
Atarra P. G. College, Atarra (Banda)

# CONTENTS

*Acknowledgement* – ***(i – ii)***

*Preface* – ***(vi – vii)***

*Glossary of symbols* – ***(viii – ix)***

***Chapter I: General Introduction*** ***01-79***

1.1 Introduction

1.2 Methods of preparation of cyanonitrosyl Complexes.

1.3 Physical studies of cyanonitrosyl complexes of Transition Metals.

1.4 Reactivity of coordinated nitric oxide.

1.5 Scope of the work

References

***Chapter II:*** ***Synthesis and structural investigations of coordination compounds of Chromium(I) with Uracil, Uracil-4-carboxylic acid and 4-Aminouracil.*** ***80-110***

2.1 Introduction
2.2 Experimental
*a)* Material Employed
*b)* Analysis of the Constituent Elements
*c)* Physical Methods
2.3 Preparation of parent compound
2.4 Preparation of complexes
2.5 Properties of complexes
2.6 Result and discussion
2.7 Summary

***Chapter III:*** ***Synthesis and structural investigations of coordination compounds of Chromium(I) with 5-Flourouracil, and 5-Methyluracil.*** ***111-132***

3.1 Introduction
3.2 Experimental
*a)* Material Employed
*b)* Analysis of the Constituent Elements
*c)* Physical Methods
3.3 Preparation of parent compound
3.4 Preparation of complexes
3.5 Properties of complexes
3.6 Result and discussion
3.7 Summary

***Chapter IV:*** ***Synthesis and structural investigations of coordination compounds of Chromium(I) with Imidazole, 1-Methylimidazole and 2-Methylimidazole.*** ***133-172***

4.1 Introduction

4.2 Experimental

***a)*** Material Employed

***b)*** Analysis of the Constituent Elements

***c)*** Physical Methods

4.3 Preparation of parent compound

4.4 Preparation of complexes

4.5 Properties of complexes

4.6 Result and discussion

4.7 Summary

***Chapter V:*** ***Biochemical Studies of synthesized coordination compounds of Chromium (I).*** ***173-188***

***Bibiliography*** ***189-205***

▪▪▪▪▪▪▪▪▪

# PREFACE

The investigation on mixed–ligand cyanonitrosyl complexes of chromium in its unusual oxidation state, +I, embodied in this thesis has been carried out in coordination chemistry laboratory at Atarra P. G. College, Atarra (Banda).

Extensive studies appears to have been made on synthesis and stereochemistry of nitrosyl complexes of Iron, Cobalt, Molybedenum, Ruthenium, Rhodium, Tungsten and Osmium, etc. But however, little work seems to have been reported on the synthesis and stereochemical aspects of cyanonitrosyl complexes of chromium in monovalent oxidation state. It is in this objective, that is to enrich nitrosyl chemistry of chromium, an attempts have been made to synthesize and characterize some mixed–ligand cyanonitrosyl complexes of chromium in +I oxidation state, and the results of this investigation are incorporated in this thesis.

The thesis entitled, **"The Synthesis and Structural Studies of Coordination Compounds of Chromium (I) with substituted Uracil and Imidazoles."** Consists of five chapters and the contents of each chapter are as follows:–

The **chapter I** begin with the general introduction in which the existing literature from the cyanonitrosyl complexes of transition metals has been briefly surveyed, followed by their bonding nature and structural aspects. As an out come of these, the scope of the present work has also been stressed.

**Chapter II** deals with the synthesis of cyano nitrosyl $\{CrNO\}^5$ coordination compounds of Chromium (I) with Uracil, Uracil–4

carboxylic acid and 4–amino uracil. The properties of the synthesized compounds have been studied in detail and the probable structures discussed on the basis of various physico–chemical analyses.

**Chapter III** describes the preparations, properties and structures of some mixed–ligand cyano nitrosyl Coordination Compounds of Chromium (I) with 5–Fluoro uracil and 5–methyl uracil.

**Chapter IV** deals with the syntheses and structural investigations of some novel cyanonitrosyl $\{CrNO\}^5$ coordination compounds of chromium (I) with Imidazole, 1-methyl imidazole and 2–methyl imidazole.

In **Chapter Vth**, that is, last chapter describes the biochemical studies of NO and synthesized coordination compounds of Chromium (I). The references given in this thesis are covered up to date.

# GLOSSARY OF SYMBOLS

| | |
|---|---|
| Å | : Angstrom unit, $10^{-10}$ m |
| β | : Beta |
| γ | : Gama |
| χ | : Magnetic susceptibility |
| $\Lambda_M$ | : Molar conductance |
| ε | : Molar extinction coefficient |
| ν | : Stretching frequency |
| δ | : Bending frequency |
| $\mu_{eff}$ | : Effective magnetic moment |
| acac | : Acetyl acetone |
| Diars | :O–phenylenebisdimethylarsine |
| dipy | : 2, 2–dipyridyl |
| DMF | : Dimethyl formamide |
| DMSO | : Dimethyl sulphoxide |
| ESR | : Electron Spin Resonance |
| Et | : Ethyl= |
| IR | : Infrared |
| L | : Ligand |
| Me | : Methyl |

| | |
|---|---|
| MO | : Molecular orbital |
| NCS | : Thiocyanate |
| NMR | : Nuclear magnetic resonance |
| CNDO | : Complete Neglect of Differential Overlap |
| Ph | : Phenyl |
| TMS | : Tetra Methyl Silane |
| Url | : Uracil |
| 4–A Url | : 4–Amino Uracil |
| Url–4CA | : Uracil 4–Carboxylic Acid |
| 5–F Url | : 5–Fluoro Uracil |
| 5–M Url | : 5–Methyl Uracil |
| Imd | : Imidazole |
| 1-M Imd | : 1–Methly Imidazole |
| 2–M Imd | : 2–Methly Imidazole |

# CHAPTER I

## *General*

## *Introduction*

# CHAPTER I

## 1.1 INTRODUCTION

Chromium, molybdenum and tungsten are the transition metal members of group VI of the periodic table. chromium has the outer electronic configuration $3d^5 4s^1$ and forms compounds in oxidation states –II to + VI (Table 1.1). It differs in its chemistry from molybdenum and tungsten, which are alike because of their similar atomic and ionic radii. Most resemblances are in the 0 and I oxidation states, which are stabilized by π–acceptor C, N heterocyclic and P donor ligands. The extensive organometallic chemistry of Cr, Mo and W is described in the companion series "Comprehensive Organometallic Chemistry"**(1a).**

Co-ordination compounds of transition metals containing nitric oxide **(1, 2)** had been known for over a century and since then nitrosyl chemistry continues to be a source of interest to chemists. However, in comparison to the related metal carbonyl complexes, they are not investigated thoroughly investigated in past due to following reasons:

**(i)** The majority of metal carbonyl synthesis is based on the use of carbon monoxide itself. Excess CO is seldom detrimental in these reactions, and high pressure, high temperature conditions are

always available for kinetically sluggish transformations. In contrast, these later conditions are seldom tolerable with nitric oxide due to its thermodynamic instability **(3)** (equation 1 & 2) and its tendency to function as an oxidizing agent.

$$3NO \rightarrow N_2O + NO_2 \quad H = 32.7 \text{ Kcal/mole} \quad \ldots\ldots \textbf{(1)}$$

$$NO \rightarrow \tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 \quad H = 21.6 \text{ Kcal/mole} \quad \ldots\ldots \textbf{(2)}$$

These limitations have motivated the development of new approaches for introducing NO group into metal complexes (vide infra).

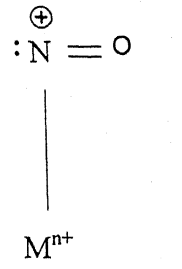
**(ii)** Another reason for this inattention was almost certainly their apparent lack of reactivity. On the one hand, M-NO bond is very strong, and the ligand displacement reactions, which are so important in the chemistry of metal carbonyl complexes, were not found in the metal nitrosyl complexes.

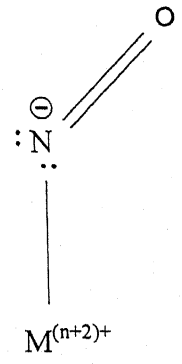
Recently, there has been a considerably interest in the study of transition metal nitrosyl complexes and the reactions of the nitrosyl ligand. This is partly due to increase in understanding of the way in which NO binds to a metal, which is subtly different to the situation involving CO, principally, because NO has an addition electron donor, giving $NO^+$, or an electron acceptor, giving $NO^-$ and even $N_2O_2$. Another stimulus to investigating NO reactivity has been the developments in pollution control **(4)**, largely stemming from attempts to remove, or at least diminish the concentration of NO in exhaust gases, emitted by the internal combustion engine. Further interest has arisen from the possibility of producing organonitrogen compounds from NO in reactions assisted or moderated by transition metal catalysts **(4)**.

The mode of bonding of coordinated NO and CO had long been considered as a strictly analogous and in that sense CO, $CN^-$, $NO^+$ and $N_2$ are isoelectronic ligands, coordinate in a similar manner because they have same external electronic configuration. Recently it has become clear that NO can bind to metals in modes not yet observed for CO. The binding in nitrosyl complexes in the simplest form is assumed, as an electron transfer from NO to the metal, proceeds the coordination of $NO^+$ through the nitrogen lone pair. Back donation from the metal to the antibonding orbital of the $NO^+$ reinforces the lone electron pair donation of the nitrogen. In this sense NO functions as a three electron donor compared to other isoelectronic ligands, e.g. CO, CN and $N_2$ which are formally two electron donors **(5-8)**.

In this mode of bonding several attempts were made to interpret the wide region of 1950-1100 $cm^{-1}$ nitrosyl stretching in infrared spectral studies. To cover the lowest range of nitrosyl stretching for the red isomer of $[Cr(NH_3)_5(NO)]^{2+}$ , it was argued that there was a transfer of an electron from the metal to NO, $NO^-$ then acting as a normal ligand with the donation of two electrons to the metal **(9)**. However, the red isomer of $[Cr(NH_3)_5(NO)]^{2+}$ was latter found to have a quite different structure which is dimeric cation, $\{[Co(NH_3)_5]_2(N_2O_2)\}^{4+}$, where the hyponitrite ion is asymmetrically bonded to the two cobalt moiety in a trans-arrangement. The long search for $NO^-$ complex predicted as early as 1934 by Sidgwick culminated in the complex, $[Ir(Cl)(CO)(NO)(Ph_3)_2]$ $BF_4$. In this case $NO^+$ is believed to be coordinated as a lewis acid, accepting an electron pair from the weak base iridium(I). In other words, the coordinated nitrosyl

group can be treated as $NO^-$ in the formal oxidation state of iridium as +3. In other words two canonical forms may be depicted as follows.





Thus, it is generally assumed that in the bent form of coordinated NO (when NO is coordinated as $NO^-$), it functions as one electron donor.

Besides these two extreme formulations of terminal bonding of nitrosyl group, the nitrosyl group like CO, can form bridges between two or three metal atoms, for example, it acts as a doubly bridging group in the compound, $[(\eta^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}NO)(\mu\text{-}NH_2)Cr(NO)(\eta^5\text{-}C_5H_5)]$ **(10)**. This is formed by the attack of borohydride upon $[Cr(\eta^5\text{-}C_5H_5)(Cl)(NO)_2]$. NO can act even as triply bridging group as has been observed in the complex $[Mn_3(\eta^5\text{-}C_5H_5)_3(NO)_4]$ **(11)**.

Cyanonitrosyl complexes have drawn a distinction from other metal nitrosyl complexes, although they are not basically

different from other nitrosyl complexes. Among these, $[M(CN)_5NO]^{n\pm}$ species have received special attention. A survey on the existing literature suggests formation of these species from different transition metals as shown in table 1.1

**Table 1.1**

**Oxidation States and Stereochemistry of Chromium**

| *Oxidation state* | *Coordination number* | *Stereochemistry* | *Examples* |
|---|---|---|---|
| $Cr^{o}$, $d^6$ | 6 | Octahedral | $Cr(bipy)_3$,$Cr(PF_3)_6$,$Cr(CNBu1)_6$ |
| $Cr^{I}$, $d^5$ | 6 | Octahedral | $[Cr(CNPh)_6]^+$, $[Cr(bipy)_3]$ |
| $Cr^{II}$, $d^4$ | 3 | Distorted 'T' | $Cr(OCBu^t_3)_2.LiCl(THF)_2$ |
| | 4 | Planar | $Cr\{N(SiMe_3)_2\}_2(THF)_2$, $Cr(acacen)$,$[Net_4]_2[Cr(S2C2H_4)_2]$ |
| | | Distorted tetrahedral | $Cr(NO)\{N(SiMe_3)_2\}_3$,$CrCl_2(MeCN)_2$ |
| | 5 | Trigonal bipyramidal | $[CrBr\{N(CH_2CH2NMe_2)_3\}]^{2+}$, $Cr_2(S_2CNEt_2)_4$ |
| | | Square pyramidal | $[Cr(NH_3)_4H_2O]^{2+}$ |
| | 6 | High–spin(distorted octahedral) | $[Cr(en)_3]^{2+}$, $[CrCl_4]_n^{2n-}$ |
| | | Low–spin(octahedral) | $[Cr(phen)_3]^{2+}$, $[Cr(CN)_6]^{4-}$ |
| | | $(Cr{\equiv}Cr)^{4+}$ units | $[Cr_2(O_2CMe)_4(H_2O)_2]$, WW$[Cr_2(2–(O), 6–Mepy)_4]$ |
| | 7 | Tetragonal base: trigonal cap(4:3) | [Cr(CNBut)7]2+ |
| | | Pentagonal bipyramidal | $CrH_2\{P(OMe)_3\}_5$ |
| $Cr^{III}$, $d^3$ | 3 | Trigonal planar | $Cr(NPr_2)^3$ |
| | 4 | Tetrahedral | $[CrCl_4]^-$? |
| | 5 | Trigonal bipyramidal. | $CrCl_3(NMe_3)_2$ |
| | 6 | Octahedral | $[Cr(NH_3)_6]^{3+}$, $Cr(acac)_3$, $[Cr(CNPh)_6]^{3+}$ $[CrC_5H_3N(CMeNNHCONH_2)_2(H_2O)_2]^{3+}$ |
| | 7 | Pentagonal bipyramidal | |
| $Cr^{IV}$, $d^2$ | 4 | Tetrahedral | $[Cr(OBut)_4$, $CrO_4^{4-}$, $CrCl_4$ |
| | 5 | Square pyramidal | CrO(TPP) |
| | 6 | Octahedral | $[CrF_6]^{2-}$ |
| | 7 | Pentagonal bipyramidal | $Cr(NH_3)_3(O_2)_2$ |
| | 8 | Dodecahedral | $CrH_4(PMe_2CH_2CH_2PMe_2)_2$ |
| $Cr^{V}$, $d^1$ | 4 | Tetrahedral | $CrO_4^{2-}$ |
| | 5 | Square pyramidal | $[CrOCl_4]^-$, CrN(salen), $[Cro(O_2COCMeEt)_2]^-$ |
| | | Trigonal bipyramidal | $CrF_5$ |
| | 6 | Octahedral | $[CrOCl_5]^{2-}$ |
| | 8 | Dodecahedral | $[Cr(O_2)_4]^{3-}$ |
| $Cr^{VI}$, $d^0$ | 4 | Tetrahedral | $CrO_4^{2-}$, $CrO_2Cl_2$, $Cr(NBut)_2(OSiMe_3)_2$ |
| | 5 | Pentagonal pyramidal | $CrO(O_2)_2py$ |
| | 6 | Octahedral | $CrF_6$, $[CrO_2F_4]^{2-}$ |
| | 7 | Pentagonal bipyramidal | $CrO(O_2)_2(bipy)$ |

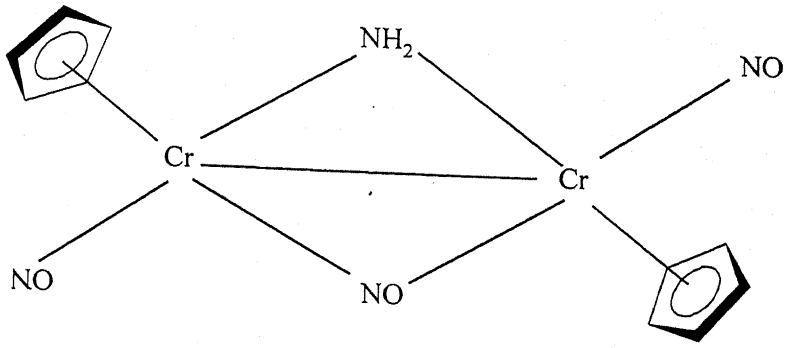



**Fig. 1**

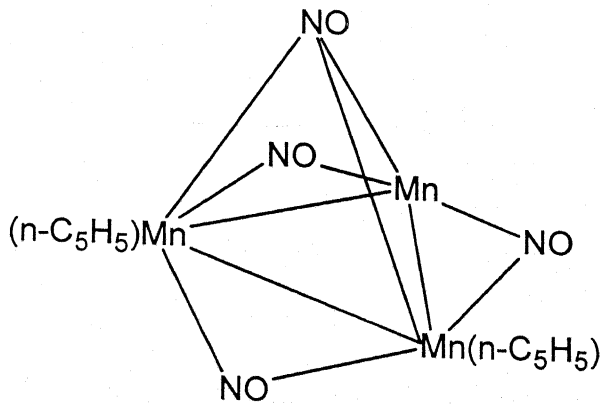



**Fig. 2**

In other stereochemistry, nickel forms $[Ni(NO)(CN)_3]^{2-}$ of tetrahedral geometry **(12)**, and vanadium gives $K_4[V(NO)(CN)_6]$ of pentagonal bipyramidal geometry **(13, 14)**. A diamagnetic cyanonitrosyl complex of composition $Ag_3[Re(CN)_7(NO)]$ is also reported **(15)**. A dimeric cyanonitrosyl complex manganese of

composition $[Mn(NO)_2(CN)_2]_2^{4-}$ has been reported by H. Behrones and coworkers **(16)**. Reduction of this compound with potassium in liquid ammonia gives another compound of composition $[Mn(NO)_2(CN)_2]_2^{4-}$ . An interesting nitrosyl complex of iron, $[Fe(NO)_2(CN)_2]^{1-}$ is reported to be synthesized from the reaction of $[Fe(NO)_2(X)]_2$ (X=halide, and cyanide ion) **(17)**. This red brown compound on further reduction with sodium amalgam gives gray green, $[Fe(NO)_2(CN)_2]^{2-}$ . Two compounds of cobalt in tetrahedral stereochemistry, such as $K_3[Co(NO)(CN)_3]$ and $Na[Co(NO)_2(CN)_2]$ also been reported **(18)**.

M. A. Zolfigol et. al. synthesized a new form of heterogeneous system for azoles and investigated a number different conditions based upon the in situ generation of $NO^+$ **(19)**. Studies on the application of $N_2O_4$, metal nitrate, dinitrogen tetraoxide complex and complexation of transition metals with macrocyclic ether.

Recently, the first synthetic SR ($Fe^{III}$)-NO complex was prepared and characterized by with the application of spectroscopic (UV-visible, EPR and IR) and electrochemical methods **(20)**. The studies revealed that NO coordinates reversibly to the $Fe^{III}$ center of SR in benzene solution and the thiolate ligand does not undergo modification during this process the recently SR-NO complex exhibits ν(N-O) and ν(Fe-N) modes very close to those of natured heme-thiolate containing enzymes and differs from those of heme-imidazole containing enzymes **(21)**.

A series of hexa-coordinated mixed ligand isothiocyanatonitrosyl $\{CrNO\}^5$ complexes of chromium(I) of the

type $[Cr(NO)(NCS)_2(L)_2H_2O)]$ have been synthesized by Maurya et al. with appropriate biologically active organic compounds **(22)**.

## 1.2 METHODS OF PREPARATION OF CYANONITROSYL COMPLEXES.

The cyanonitrosyl complexes were synthesized using typically different methods. Each method is suitable for a particular transition metal as summarized below:

**(a) Preparation of nitrosyl complexes involving substitution of cyano groups in the cyanonitrosyl complexes:**

Sarkar and Maurya **(23)** reported the preparation of some cationic dinitrosyl complexes of Vanadium in oxidation state (I) by taking parent compound $K_3[V(CN)_5(NO)].2H_2O$ with orthophenanthroline/dipyridyl in 1:4 mole ratio and shaking for 24 hrs. The red violet coloured compounds so precipitated were of compositions, $[V(NO)_2(o\text{-}phen)_2].CN$ and $[V(NO)_2(dipy)_2].CN$, respectti-vely. The same authors synthesized some compounds of composition $[V(CN)_4(L\text{-}L)(NO)]^{2-}$, where L-L = o-phen or dipy, by taking $K_4[V(CN)_6NO]$ in aqueous medium and the organic ligand dissolved in ethanol in a reaction vessel, after continuous stirring of the reaction mixture around 35-40°C under nitrogen atmosphere. The compounds of aforesaid compositions as yellow mass were obtained.

Maurya and co-workers **(24)** have reported the synthesis of some novel cyanonitrosyl complexes of

chromium (I) by the interaction of pentacyanonitrosyl-chromate (I) with different nitrogen, oxygen and sulfur donor ligands in aqueous acetic acid medium. On the basis of different physico- chemical studies suitable structures have been proposed.

A molybdenum (0) nitrosyl complex of composition $[Mo(NO)_2(CN)_2(phen)].2H_2O$ has been investigated by Bhattacharya et al **(25)**. They prepared this compound by adding hot aqueous solution of phenanthroline into freshly prepared solution of $[Mo(NO)_2(CN)_4]^{2-}$ with stirring at 60°C.

**(b) Alkaline hydroxylamine method:**

Hieber and co-workers first employed the use of hydroxylammonium chloride as nitrosyl agent **(26)** tracing back an observation made by Vonderheide and Hofmann **(27)**. The use of hydroxylamine in the synthesis of metal nitrosyl utilizes hydroxylamine in the basic solution. Molybdate, cyanide and KOH react with hydroxylamine hydrochloride in aqueous medium to give a violet product of composition, $K_4[Mo(NO)(CN)_5].2H_2O$ **(28)**. There was some controversy to formulate this compound and an alternate octa-coordinated structure, $K_4[Mo(NO)(OH)_2(CN)_5]$ was proposed by Griffith, Lewis and Willkinson **(28)**. X-ray studies finally confirmed the hexa-coordinated structure and the composition of the compound is really $K_4[Mo(NO)(CN)_5].2H_2O$. The complex is also accessible directly from $K_4[Mo(CN)_6]$ **(25)**. Willkinson and co-workers then utilized this procedure on other oxometallate anions.

Thus with $CrO_4^{2-}$, the green complex, $K_3[Cr(NO)(CN)_5].H_2O$ was isolated **(29)**. Bhattacharya and co-workers reported the preparation of $K_3[Re(CN)_5(NO)].2H_2O$ by taking perrhenate(VII), $ReO_4^-$, excess of $CN^-$, KOH and hydroxylamine hydrochloride ($NH_2OH.HCl$). The same authors **(30)** reported the preparation of some new molybdenum(II) cyanonitrosyl complexes, $R_2[Mo(NO)(CN)_5].2H_2O$ (R = $Ph_4P$ or $Bu_4N$) using $Na_2MoO_4.2H_2O$, KCN, and $NH_2OH.HCl$ in alkaline medium maintaining pH 8.

Ammonium vandate ($NH_4VO_3$), cyanide and base react with hydroxylamine to produce a vanadium nitrosyl **(31)**, originally formulated erroneously as $[V(NO)(CN)_5]^{5-}$. This has been characterized structurally **(32)** as $[V(NO)(CN)_5]^{3-}$. When this reaction is performed under $H_2S$, the product was claimed to be $K_4[V(CN)_6NO].H_2O$; although the CN and NO stretching frequencies closely resemble those of $[V(NO)(CN)_5]^{3-}$ the cell constant differ and the compound is diamagnetic **(33)**.

The source of nitrosyl group in the alkaline hydroxylamine medium has been attributed to the following sequence of purely formal reaction **(34-36)**.

$$2\,NH_2OH \longrightarrow NH_3 + NOH + H_2O$$

$$NOH \longrightarrow NO^- + H^+$$

Basic conditions are suggested to be required to displace the second reaction toward "$NO^-$.

**(a) The reaction of nitric oxide on a cyano complex of a transition metal:**

Nitric oxide reacts with $K_4[Ni(CN)_6]$ in liquid ammonia suspension to form a deep violet $K_2[Ni(CN)_3(NO)]$ **(26)**.

**(b) The reaction of nitric acid on a cyano complex of a transition metal:**

This method has been first employed for preparation of sodium pentacyanonitrosylferrate(II), commonly called sodium nitroprusside, by nitric acid on sodium hexacyanonitrosylferrate(II), $Na_4[Fe(CN)_6]$ **(37)**. The same method has been applied for the preparation of analogous ruthenium and osmium complexes **(38)**. The treatment of $Na_3[Re(CN)_5(H_2O)]$ with moderately strong nitric acid is reported to yield a cyanonitrosyl complex of rhenium having composition $Na_2[Re(CN)_5(NO)]$ **(39)**. A diamagnetic cyanonitrosyl complex of rhenium of suggested composition, $Ag_3[Re(CN)_5(NO)]$ (contaminated with AgCN), obtained when $K_3[Re(CN)_8]$ was warmed with 2 molar nitric acid.

**(c) Preparation using redox reactions:**

In the preparation of nitrosyl compounds the use of nitric acid as nitrosylating agent has been successfully

applied to the synthesis of nitroprusside and its ruthenium and osmium analogous, in the same formal oxidation state, i.e. +2. Although oxidation state of the central metal ion attached with NO has got no sense in the real sense of the term, yet a formalism containing $(MNO)^{n+}$ would avoid an extreme formalism of either as $NO^+$ or $NO^-$ (vide infra). In this sense, by following the same process of preparation, Fe Ru and Os give $(MNO)^{3+}$ in their complexes. Contrary to this using hydroxylamine method of preparation, chromium gives $(CrNO)^{2+}$ group whereas molybdenum gives $(MoNO)^+$ moiety. This prompted Griffith **(34)** to reduce the $(CrNO)^{2+}$ containing compound, $K_3[Cr(NO)(CN)_5]$, (using polarographic method of reduction) to isolate a blue reduced species, $K_4[Cr(CN)_5(NO)].H_2O$, analogous to $K_4[Mo(CN)_5(NO)]$. There has been several attempts to isolate one oxidation product of $K_4[Mo(CN)_5(NO)]$ to obtain, but the pure green product **(40, 41)** was isolated only by Sarkar and co-workers **(40)** using air as oxidizing agent. Similarly the purple coloured complex $K_3[Mo(CN)_5(NO)].2H_2O$ **(42)** on oxidation with bromine or nitric acid gives yellow $K_2[Mo(CN)_5(NO)].2H_2O$. The reduction of sodium nitroprusside with sodium in liquid ammonia yields other yellow compound $Na_3[Fe(NO)(CN)_5].2NH_3$ as an unstable solid **(43)**. The corresponding tetraethylammonium salt, when treated with acetic acid in acetonitrile converts it into a blue coloured complex **(44)** $(Et_4N)_2[Fe(NO)(CN)_4]$.

Gray green **(45)** $[Fe(NO)(CN)_2]^{2-}$ has been prepared by the sodium amalgam reduction of paramagnetic red-brown $[Fe(NO)_2(CN)_2]^{1-}$. $[Mn(NO)_3(CO)]$ reacts with KCN in liquid ammonia to give a deep yellow diamagnetic anion, $[Mn(NO)_2(CN)_2]^{4-}$ having a metal-metal bond. Reduction of this complex with potassium in liquid ammonia gives the unstable product **(46)** $[Mn(NO)_2(CN)_2]^{3-}$.

## 1.3 PHYSICAL STUDIES OF CYANONITROSYL COMPLEXES OF TRANSITION METALS.

As the emphasis in this thesis is made on the preparation and characterization of some mixed ligand cyanonitrosyl complexes involving simple and biologically important organic compounds, which were explored using some substitution reactions. Hence it is proper to discussed briefly different physical methods used so for, for the elucidation of structural aspects of the starting complexes of the other transition metals. The shapes of the complex ions are of great interest which can account for in indication of the relative strength of chemical reactivities on these complexes (vide infra). Therefore, some general comments on results of X-ray diffraction studies, magnetic measurement along with ESR, vibrational, electronic, photoelectronic and mass spectra, redox properties and kinetic studies are reviewed here.

### The $\{M(NO)_m\}^n$ formalism

Before going to the different physical studies pertaining to structure and bonding of nitrosyl complexes, one must be aware about the inorganic functional group

notation for nitrosyl complexes. For understanding the complex behaviour of metal nitrosyl compounds, these are conveniently classified as derivatives of the appropriate inorganic functional group $\{M(NO)_m\}^n$, e.g. $\{M(NO)\}^n$, $\{M(NO)_2\}^n$, $\{M(NO)_3\}^n$: the value of n corresponds to the number of 'd' electrons on the metal, when the nitrosyl ligand is formally is considered to be bound as $NO^+$.

**(i) Electron spin resonance studies:**

Most of the work in this field is related with the investigation of ESR spectrum of the $[Cr(NO)(CN)_5]^{3-}$. Several groups **(48-56)** have tried to interpret spectrum, but there is no complete agreement on the interpretation of the observed data. As an account of these investigations, the important experimental results may be summarized as below:

(a) The 'g' and chromium hyperfine tensor has slight deviation from axial symmetry.

(b) The nitrogen hyperfine tensor has slight deviation from axial symmetry, which may be comparable to the deviation observed for the CrNO group.

(c) The nitrogen hyperfine tensor is highly anisotropy and $g_{||} < g_{\perp}$.

The ESR parameters for other hexa-coordinated complexes of the family $[Cr(NO)L_5]$ **(57-64)** are as expected and depend on the electronegativity of L. The 'g' value comes closer to free electron value when there is more

delocalization. This is also reflected in NO stretching frequency.

The acid hydrolysis of $[Cr(NO)(CN)_5]^{3-}$ has been followed by ESR method **(65)**, by which it can be shown that the successive replacement of cyanide groups by water takes place.

Sometimes, ESR spectroscopy can firmly predict the stereochemistry of a complex. This has been exemplified by the study of the oxidized species, $[Mo(NO)(CN)_5]^{3-}$, which was not isolated at the time **(40)**, but the ESR. parameters obtained for the oxidized species in the host $K_3[Co(CN)_6]$ supports the formation of parent $d^6$- diamagnetic complex as $[Mo(NO)(CN)_5]^{4-}$ rather than $[Mo(NO)(CN)_5(OH)_2]^{4-}$, which was later verified by X- ray studies. The ESR studies on $[Mn(CN)_5\ (NO)]^{2-}$ has been studied in detail **(66-69)** because of the interest in the ordering of he energy level in the corresponding Cr(I) and Fe(II) complexes. There is controversy existed to attribute the spin density in the NO group, where one group believes this due to spin orbit coupling, whereas the other group feels that the spin polarization mechanism is most likely.

Surprisingly, radiation of the diamagnetic $K_3[Mn(NO)(CN)_5]$ **(68)** produced the oxidized $[Mn(CN)_5(NO)]^{2-}$ species by simple electron addition, whereas nitroprusside looses an electron on irradiation.

## (ii) Magnetic Measurement Studies:

An advanced understanding of the bonding scheme of nitrosyl complexes is required for the theoretical knowledge of the magnetic properties of the nitrosyl complexes. Hence various bonding scheme based on the molecular orbital approach developed, so far, would be reviewed here.

The X-ray structural results allow a quantitative picture of the bonding in transition metal nitrosyl to be derived. However, molecular orbital calculations carried out in attempts to place the bonding in nitrosyl complexes on a more quantitative basis.

Johnson and McCleverty have reviewed the molecular orbital calculations carried out by Manoharan and Gray **(70)** on the pentacyanonitrosyl compounds $[Mn(CN)_5(NO)]^{n-}$. The energy level scheme derived by them are presented in Fig. 1.1

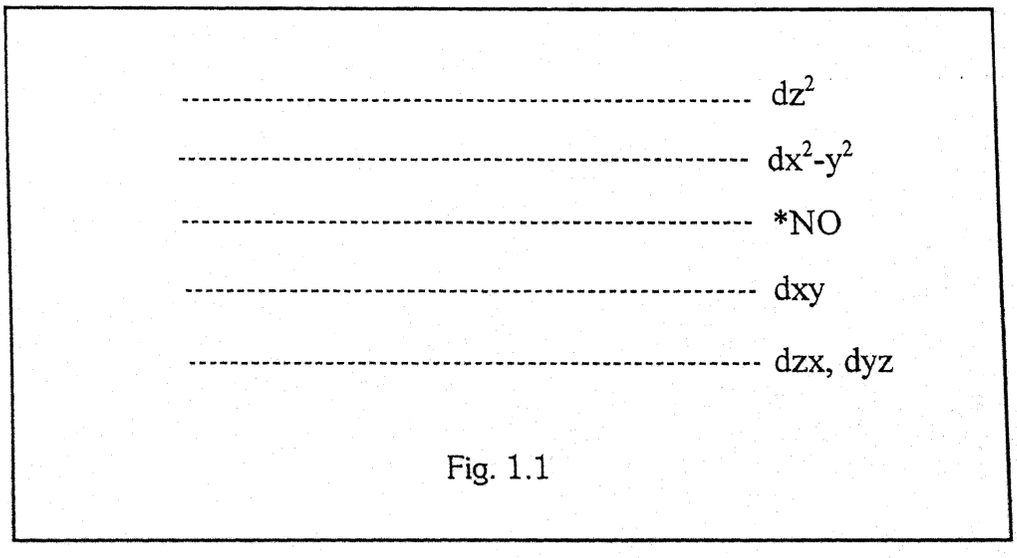



Fig. 1.1

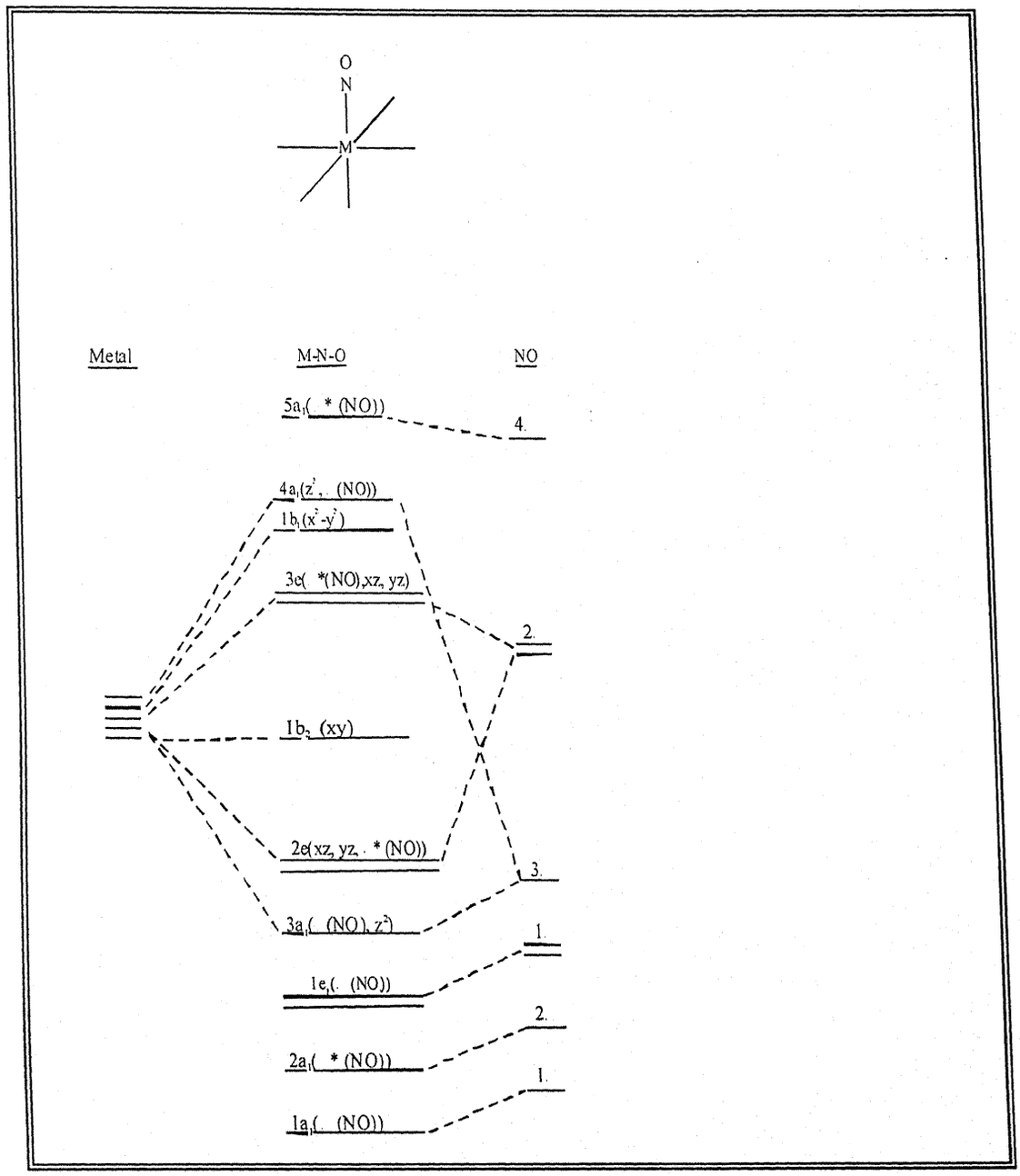



***Fig. 1.2 The molecular orbital diagram for six coordinate complexes with linear MNO groups. The z axis is coincident with the M-N-O bond.***

It has been used as a basis for quantitative bonding discussion for other complexes of general formula, $[M(NO)L_5]^{n+}$, where L are ligands such as $NH_3$ and $H_2O$. A certain amount of controversy **(71-73)** over the ordering of the $d_z^2$ and $d_{x^2-y^2}$ levels of the Gray's scheme still exists.

J. H. Enermark and R. D. Feltham **(74)** developed an alternative description of the bonding in metal nitrosyl complexes utilizing the molecular orbital correlation method. For six coordinated complexes of the MNO group, where maximum symmetry is $C_{4v}$, the molecular orbital diagram derived by them is presented in Fig.1.2. The important features of this molecular diagram are as follows:

The orbital $3a_1$ is primarily localized on the N atom of the NO ligand and is $\sigma$ - bonding with respect to the MNO group. The degenerate 2e orbital, consisting primarily of the metal $d_{xz}$, $d_{yz}$ and the $\pi^*$ orbital of the NO ligand, is bonding with respect to M and N is antibonding between N and O. The $1b_2$ orbital is localized on the metal ($d_{xy}$) and is non bonding. Thus an MNO complex with the electronic configuration $(3a_1)^2(2e)^4$ has three bonding interactions between the metal and the NO group. This situation corresponds to the usual back bonding model used in describing the bonding of $NO^+$ or CO with transition metals. The presence or absence of electrons in the $1b_2$ orbital will be of minor consequence as far as the MNO group concerned.

In advancement of the bonding scheme of nitrosyl complexes, the observed magnetic moment values are quite expected. Taking into account, the metal and nitrosyl group together (because of the fact that nitric oxide is itself is paramagnetic with respect to one unpaired electron), the number of the total electrons present in this group are given in Table 1.2, along with the expected number of unpaired electrons and the observed magnetic moment values. The strong covalent nature of M-NO bonding is now certain from the studies of the physico-chemical measurements and X-ray structural analysis. The bonding scheme presented in Fig.1.2 shows the nature of this interaction. Though cyanide group in most of its complexes behave as a good $\pi$ bonding ligand in cyanonitrosyl complexes, the strong interaction between metal ion and nitrosyl group, is enough to cause the separation of bonding, non bonding and antibonding orbitals to a large extent. In these hexacoordinated complexes maximum symmetry expected is $C_{4V}$ leading to a strong tetragonal distortion. Thus the ordering of these orbitals according to Fig.1.2 is $(2e) < (1b_2) < (3e)$. The bonding orbitals below 2e will accommodate the ligand electrons. Thus filling up of the 'd' electrons on the metal will start from '2e' level. Rationalization of the bonding scheme has been done mainly on the consideration that the nitrosyl ligand is as $NO^+$.

It is convenient to classify MNO complexes by the number of d electrons present in the complex. Thus an MNO complex with electronic configuration $(3a_1)^2(2e)^4$ would be

method of designating the number of d- electrons present in MNO complexes corresponds to the familiar number of d-electrons on the metal when the nitrosyl ligand is formally considered to be $NO^+$. In this formalism the cyanonitrosyl complexes may contain the electronic configuration $\{MNO\}^n$, where the value of n may be 4, 5, 6 or 7, which directly count the number of d electrons. Obviously complexes containing n=4 or 6 will show diamagnetism and n=5 or 7, paramagnetism with respect to one unpaired electrons, is expected. The magnetic moment values are presented in Table 1.2. For the complexes containing $d^5$ configuration, the spin orbit coupling constant would contribute in the measured magnetic moment value. The spin orbit coupling constant for Mo(I), Mn(II) and Cr(I) are 450, 300 and 190$cm^{-1}$ respectively, which will affect the magnetic moment values a bit greater than the spin only value at room temperature. The observed result for the Cr and Mo complexes described hare follow this trend. However, for the maganese complex the magnetic moment measurement of $K_2[Mn(NO)(CN)_5]$ in the solution gives the value corresponding to spin only formula. Interestingly the magnetic moment value of its silver salt, measured in the solid state gives a sub normal magnetic moment of 0.55 B.M. only **(41)**. The reason for this anomaly is difficult to explain. The last two compounds given in Table 1.2 also show unusually low magnetic moment due to the polymeric nature of the complexes **(46)**.

### *(iii) Electronic Spectra*

Data for Chromium (I) complexes are sparse. However, the spectra of some nitrosyl derivatives have been reported **(70, 73 & 75)**. In the system $[Cr(I)L_5NO]^{n-}$ (L= CN, $NH_3$), the sequence of energy level is purported to be:

$e(xz, yz) + \pi (NO^+) < b_2(xy) < e(\pi^*NO^+) < b_1(x^2-y^2) << a_1(z^2)$

Where there is an important interaction between the xz, yz orbitals of the metal and the $\pi$ orbitals of the nitrosyl group, assumed to be $NO^+$. For L = CN, three bands are seen at 13,700, 22,200 and 27,320 $cm^{-1}$, while for L = NH3, the bands occur at 17,480, 22,200 and 28,170 $cm^{-1}$. Upon cooling the cyanide complex, the first two bands show no change in the intensity, while third decreases in intensity. In the case of ammonia derivative, the first peak does not change in intensity on cooling, but the second and third bands do.

*Table 1.2*

| Compound | Electron configuration $MN^{n*}$ | Expected number of unpaired electron(s) | Expected magnetic moment (spin only value) (B.M.) | Observed magnetic moment (B.M.) | Reference |
|---|---|---|---|---|---|
| $K_3[VNO(CN)_5].2H_2O$ | $\{VNO\}^4$ | 0 | 0 | D | **32** |
| $K_4[VNO(CN)_6].2H_2O$ | $\{VNO\}^4$ | 0 | 0 | D | **34** |
| $K_3[CrNO(CN)_5].H_2O$ | $\{CrNO\}^5$ | 1 | 1.73 | 1.87 | **28** |
| $K_4[CrNO(CN)_5].2H_2O$ | $\{CrNO\}^6$ | 0 | 0 | D | **37** |
| $K_3[MnNO(CN)_5].2H_2O$ | $\{MnNO\}^5$ | 0 | 1.73 | 1.73 | **41** |
| $K_2[MnNO(CN)_5].2H_2O$ | $\{MnNO\}^5$ | 1 | 1.73 | 1.73 | **41** |
| $Na_2[FeNO(CN)_5].2H_2O$ | $\{FeNO\}^6$ | 0 | 0 | D | **41** |
| $(Et_4N)_2[FeNO(CN)_5]$ | $\{FeNO\}^7$ | 1 | 1.73 | 1.75 | **42** |
| $K_4[Mo(NO)(CN)_5]$ | $\{MoNO\}^6$ | 0 | 0 | D | **26** |
| $(PPh_4)_3[MoNO(CN)_5].2H_2O$ | $\{MoNO\}^5$ | 1 | 1.73 | 1.96 | **42** |
| $[CrNO(CN)_2(dipy)]$ | $\{CrNO\}^5$ | 1 | 1.73 | 1.60 | **46** |
| $[CrNO(CN)_2(o\text{-}phen)]$ | $\{CrNO\}^5$ | 1 | 1.73 | 1.67 | **46** |

n* = Number of electron in d orbital
D = Diamagnetic

In both the cases 22,200 $cm^{-1}$ band shows significant vibrational structure with vibrational spacing of 390 – 520 $cm^{-1}$. The ground state, in $C_{4v}$ symmetry, is the low spin ($e^4b_2^1$) and the three transitions are assigned, in the case of L = CN, in increasing order of energy:

$^2E$ ----$^2B_2$ [ e(xz,yz) -------- $b_2$ (xy)] allowed in $C_{4V}$ symmetry.

$^2E$ ----$^2B_2$ [ e(xz,yz) -------- e ($\pi^*$ ($NO^+$)] allowed in $C_{4V}$ symmetry.

$^2B_1$ ----$^2B_2$ [ $b_2$ (xy) -------- $b_1$ ($x^2$-$y^2$)] forbidden in $C_{4V}$ (vibronic).

The third band energy of 27,320 $cm^{-1}$ (L = CN) which is formally equal to 10 Dq, is close to that observed for the $Cr(CN)_6^{3-}$ ion (10 Dq = 26, 600 $cm^{-1}$).

In the case of the ammonia derivative, these authors assign the structured 22,200 $cm^{-1}$ band to the $^2B_1$ ----$^2B_2$ transition since the energy is similar to 10 Dq for $Cr(NH_3)_6^{3-}$, and since, unlike the cyanide derivative, the intensity of this band decreases with cooling. However, the very close similarity in shape and structure of the 22,200$cm^{-1}$ band in two complexes argues strongly for the same assignment in both.

Two macrocycle containing chromium(I) nitrosyl derivatives have been reported by Busch and co-workers **(76)**. The sequence of energy level is proposed to be:

e(xz, yz) + $\pi$ ($NO^+$) < $b_2$(xy) < $a_1(z^2)$ < $b_1(x^2-y^2)$ < e($\pi^*(NO^+)$)

and three bands near 15,300, 22,200, and 26-28,000 are assigned to the $2_{A_1} ----2_{B_2}$, $2_{B_1} ----2_{B_2}$ and $2_E ----2_{B_2}$ transitions respectively.

Attempts to correlate the structural information with a unified description of the bonding in metal nitrosyl complexes formally remain not much of significance. This is due to the fact that, whether nitrosyl group is positive or negative. This means that how many 'd' electrons are present in the compound. Till today we do not have any formal answer to this problem regarding this formal oxidation state of the metal ion involved. It is only recently that meaningful alternative description of the bonding in metal complexes is developed. This is originated from the analysis of the structures of the triatomic species of the non-transition element using the correlation method by Walsh **(78)**, which was first developed by Hund **(79)** and Mulliken **(80)**. Walsh's study is concerned with triatomic species which has only 's' and 'p' orbitals in the valence shell of the atoms and suggested that the concept should be in general applicable. Mingos and Ibers **(81)** have first applied this concept to understand the M-N-O angles in the metal nitrosyl complexes. Pierpont and Eisenberg **(82)** and Mingos **(83)** have utilized these concepts in attempts to interprete the geometries of tetragonal metal nitrosyl complexes. In a six coordinated complexes of MNO group, the maximum symmetry is $C_{4V}$ and accordingly the modifications of the molecular orbital diagram for the linear triatomic species, MNO, will change in $[M(NO)L_5]$ as shown in Fig.1.2.

It is experimentally difficult to know the ground state configuration of the diamagnetic complexes in the series $[M(NO)L_5]$. However, E.S.R. technique has been widely employed to investigate the ground state electronic configuration of paramagnetic complexes, especially $K_3[Cr(NO)(CN)_5]$. Although there is no complete agreement on the interpretation of the E.S.R. data of this complex made by several groups, yet the successful explanation of most of the E.S.R. parameters is consistent with the assignment of $^2B_2$ ground state expected from the electronic configuration $(2e)^4(^1b_2)^1$. Manoharan and Gray **(84)**, using the information from the known crystal structure of $Na_2[FeNO(CN)_5].2H_2O$, assign the observed electronic transitions of a series of cyanonitrosyl complexes. Though the agreement between observed electronic transition energies is not very good, yet the model they have used can accommodate a wide variety of experimental facts, is interesting. The obtained results of Manoharan and Gray are shown in Table1.3.

## *Table – 1.3*
## *Electronic spectra of $[M(CN)_5NO]^{n-}$ in aqueous solution*

| Complex | Observed maximum ($cm^{-1}$) | | Calculated Energies ($cm^{-1}$) | Bend assignment | |
|---|---|---|---|---|---|
| $[V(CN)NO]^{5-}$ | 12,900 | 1.15 | 9,200 | $^1A_1 \rightarrow {}^1E$ | $(2b_2 \rightarrow 7e)$ |
| | 21,160 | 36.5 | 19,000 | $^1A_1 \rightarrow {}^1A_2$ | $(2b_2 \rightarrow 3b)$ |
| | 32,470 | 1000 | 30,100 | $^1A_1 \rightarrow {}^1A_1$ | $(6e \rightarrow 7e)$ |
| | 37,470 | 5200 | 23,260 | $^1A_1 \rightarrow {}^1E$ | $(2b_2 \rightarrow 8e)$ |
| $[Cr(CN)_5(NO)]^{3-}$ | 13,700 | 8 | 12,660 | $^2B_2 \rightarrow {}^2E$ | $(6e \rightarrow 2b_2)$ |
| | 15,380 | 1.5 | 13,890 | $^2B_2 \rightarrow {}^2B_2$ | $(2b_2 \rightarrow 2e)$ |
| | 22,200 | 72 | 26,550 | $^2B_2 \rightarrow {}^2B_2$ | $(6e \rightarrow 7e)$ |
| | 27,320 | 59 | 28,260 | $^2B_2 \rightarrow {}^2B_1$ | $(2b_2 \rightarrow {}^3b_1)$ |
| | 37,300 | 1100 | 37,420 | $^2B_2 \rightarrow {}^2E$ | $(5e \rightarrow {}^3b_2)$ |
| | 43,480 | 3600 | 35,680 | $^2B_2 \rightarrow {}^2E$ | $(2b_2 \rightarrow 8e)$ |
| $[Mn(CN)_2(NO)]^{3-}$ | 18,520 | 22.2 | 14,900 | $^1A_1 \rightarrow {}^1E$ | $(2b_2 \rightarrow 7e)$ |
| | 24,690 | 60 | 24,200 | $^1A_1 \rightarrow {}^1A_1$ | $(6e \rightarrow 7e)$ |
| | 28,980 | 111.4 | 26,500 | $^1A_1 \rightarrow {}^1A_2$ | $(2b_2 \rightarrow 3b_1)$ |
| | 37,850 | 1000 | 37,770 | $^1A_1 \rightarrow {}^1E$ | $(6e \rightarrow 5a_1)$ |
| | 42,550 | 4500 | 41,490 | $^1A_1 \rightarrow {}^1E$ | $(6e \rightarrow 3e)$ |
| | 45,450 | 5000 | 40,470 | $^1A_1 \rightarrow {}^1E$ | $(2b_2 \rightarrow 8e)$ |
| $[Mn(CN)_5(NO)]^{2-}$ | 12,050 | 19 | 7,820 | $^2B_2 \rightarrow {}^2E$ | $(6e \rightarrow 2b_2)$ |
| | 18,600 | 20 | 18,350 | $^2B_2 \rightarrow {}^2E$ | $(2b_2 \rightarrow 7e)$ |
| | 25,960 | 1700 | 26,170 | $^2B_2 \rightarrow {}^2B_2$ | $(6e \rightarrow 7e)$ |
| | 28,860 | 120 | 32,530 | $^2B_2 \rightarrow {}^2B_1$ | $(2b_2 \rightarrow 3b_1)$ |
| | 32,280 | 880 | 28,830 | $^2B_2 \rightarrow {}^2E$ | $(5e \rightarrow 2b_2)$ |
| | 37,030 | 2400 | 38,740 | $^2B_2 \rightarrow {}^2E$ | $(6e \rightarrow 5a_1)$ |
| | 48,540 | 23800 | 45,050 | $^2B_2 \rightarrow {}^2E$ | $(2b_2 \rightarrow 8e)$ |
| $[Fe(CN)_5(NO)]^{2-}$ | 20,080 | 8 | 20,540 | $^1A_1 \rightarrow {}^1E$ | $(2b_2 \rightarrow 2e)$ |
| | 25,380 | 25 | 25,090 | $^1A_1 \rightarrow {}^1A_1$ | $(6e \rightarrow 7e)$ |
| | 30,300 | 40 | 30,770 | $^1A_1 \rightarrow {}^1A_2$ | $(2b_2 \rightarrow 3b_1)$ |
| | 37,800 | 900 | 37,750 | $^1A_1 \rightarrow {}^1E$ | $(6e \rightarrow 5a_1)$ |
| | 42,000 | 700 | 37,750 | $^1A_1 \rightarrow {}^1E$ | $(6e \rightarrow 3b_1)$ |
| | 50,000 | 24000 | 4,900 | $^1A_1 \rightarrow {}^1E$ | $(2b_1 \rightarrow 8e)$ |

*(iv) Mass spectral studies:*

Mass spectral studies on nitrosyl compound have involved the measurement of physical quantities such as ionization energies **(85-87)**, metal – ligand dissociation energies **(88)** and the investigation of fragmentation patterns **(89-92)**.

For a series of compound, $[Fe(NO)_2(CO)L]$, a linear correlation is found between the first ionization energy of the corresponding ligand, L **(85-86)**. An increase in the $\pi$-bonding ability of L brings about a decrease in the first ionization energy of the complex. Calculation of the first ionization energies of $[Fe(NO)_2(CO)L]$ and $[Co(NO)(CO)L]$ have also been made **(87)** and shown to be in good agreement with the measured values.

For fragmentation patterns of $[M(NO)_2X]_n$ where X=Cl, Br & I and M=Co & Fe have been investigated **(90)**. The nitrosyl groups are removed stepwise from the iron compounds, giving $[Fe_2X_2]^+$, but the spectra of the cobalt species show higher abundancies of mononuclear ions containing nitrosyl groups. These results are said to show that the iron compounds contain metal – metal bonds which add to the stability of the dinuclear fragments.

An interesting rearrangement has been observed in the mass spectra of several organometallic nitrosyls. In the fragmentation pattern of $[CpV(NO)_2Co]$, the ion $VO^+$ is observed, and in that of $[CpFe(NO)_2]$, the ion $Cp_2FeO^+$. Meta stable peaks show that these ions are formed in the following processes.

$$[CpV(NO)]^+ \longrightarrow VO^+ + C_5H_5N$$

$$[Cp_2Fe_2(NO)]^+ \longrightarrow Cp_2FeO^+ + C_5H_5N$$

Similar rearrangements do not occur in the mass spectra of [CpNi(NO)] or $[CpM(NO)(CO)_2]$, where M= Cr, Mo and W. The different behaviour is suggested to occur because the intermediate ions, $[CpV(NO)]^+$ and $[Cp_2Fe(NO)]^+$ contain an even number of electrons, whereas $[CpNi(NO)]^+$ and $[CpM(NO)]^+$ contain an odd number of electrons.

Maurya et al. **(93)** have carried out the mass spectral study of bis (acetylacetonato)nitrosylchromium(I), $[Cr(NO)(acac)_2]$ at ionization energy 70 eV and acceleration voltage 1500 V. Besides the parent ion peak at m/z 280, fragment ions like $NO^+$, $Cr^+$, $Cr(acac)^+$, $CrNO(acac)^+$, $Cr(acac)_2^+$ and $Cr(acac)_3^+$ are also observed. On the basis of such results the compound is confirmed to be monomeric.

### *(v) Kinetic studies:*

The kinetics of the reaction of nitroprusside ion $[Fe(NO)(CN)_5]^{2-}$ with various substrate have been widely studied. The simplest reaction studied is that of the nitroprusside ion with $OH^-$ ion, which has long been known to result in the formation of $[Fe(NO_2)(CN)_5]^{5-}$. Detailed thermodynamics and kinetic investigations **(94)** suggested that the mechanism of the reaction is as follows :

$$[Fe(NO)(CN)_5]^{2-} + OH^- \rightarrow [Fe(NO_2H)(CN)_5]^{3-} \text{.....(i)}$$

$$[Fe(NO_2H)(CN)_5]^{3-} + OH^- \rightarrow [Fe(NO_2)(CN)_5]^{4-} + H_2O \text{.....(ii)}$$

The rate determining step is reaction **(i)**. The $pK_a$ value for the equilibrium,

$$[Fe(NO_2)(CN)_5]^{4-} \rightleftharpoons [Fe(NO_2H)(CN)_5]^{3-}$$

has been estimated **(95)**.

The nitroprusside ion and $SH^-$ react via a mechanism similar to that outlined above. $[Fe(NOS)(CN)_5]^{4-}$, which is unstable in solution, is formed via an intermediate which possibly contains the NOSH group **(96)**.

The deep blue solutions generated when mixture of $[Fe(NO)(CN)_5]^{2-}$ and $NCS^-$ are irradiated, may also be made by acidification of a basic solution of the two reaction **(97, 98)**. The species responsible for the deep blue colour is suggested by kinetic studies to be $[Fe(NCS)(CN)_5]^4$, formed by the reaction of $[Fe(NO_2)(CN)_5]^{4-}$ or $[Fe(H_2O)(CN)_5]^{3-}$ with thiocyanate ion. The nitrous acid present in the reaction reduces the deep blue species to the related trianion, $[Fe(NCS)(CN)_5]^{3-}$ **(99)**.

$$[Fe(CN)_5(NO)]^{2-} + H_2O \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + NO^+$$

$$\downarrow NCS^-$$

$$[Fe(CN)_5(NO)]^{2-} + NCS^- \longrightarrow [Fe(CN)_5(NCS)]^{4-} + NO_2^-$$

$$NO^+ + 2OH^- \longrightarrow NO^{2-} + H_2O$$

$$[Fe(CN)_5(NCS)]^{4-} + NHO_2 \longrightarrow [Fe(CN)_5(NCS)]^{3-}$$

An investigation **(100)** of the kinetics of the reactions of $[Fe(NO)(CN)_5]^{2-}$ with thiourea, particularly, $(NH_2)_2CS$, $(Me_2N)_2CS$ and $(EtNH)_2CS$ has allowed the following mechanism to be proposed :

$$[Fe(NO_2H_2)(CN)_5]^2 \longrightarrow [Fe(NO_2H_2)(CN)_5]^{*2-}$$

$$[Fe(NO_2H_2)(CN)_5]^{*2-} + (NR_2)_2CS \rightleftharpoons [Fe(NO_2H)(CN)_5]^{3-} + [(NR_2)_2CSH]^+$$

$$[Fe(NO_2H)(CN)_5]^{3-} + [(NR_2)_2CSH]^+ \longrightarrow [Fe\{(NR_2)_2CS\}(CN)_5]^{2-}$$

The hydrolysis of $[Cr(NO)(CN)_5]^{3-}$ has been studied by ESR (61) and electro-chemical studies **(101)**. The ESR spectra of all aquation products $[Cr(NO)(H_2O)(CN)_{5-X}]^{X-3}$ have been observed and the processes,

$$[Cr(NO)(H_2O)_3(CN)_2]^0 \longrightarrow [Cr(NO)(H_2O)_4(CN)]^+$$

and

$$[Cr(NO)(H_2O)_4(CN)]^+ \longrightarrow [Cr(NO)(H_2O)_5]^{2+}$$

Shown to be first order **(65)**.

Polarography showed that the first reaction in the sequence is also first order. The rate determining step being the loss of the first $CN^-$ ligand **(101)**. The mechanism suggested for the formation of the monoaquo complex is:

$$[Cr(NO)(CN)_5]^{3-} + H^+ \longrightarrow [CrNO.H(CN)_5]^{2-} \xrightarrow{H_2O^+} [Cr(NO)(H_2O)(CN)_4]^{2-} + HCN$$

### *(vi) X-ray diffraction studies:*

Recent X-ray structural studies revealed that although most transition metal nitrosyl contain essentially linear M-N-O bond angles, which are very close to 180°. It is useful, however, to discuss the older bonding concept before considering how nitric oxide binds to a metal in linear or bent fashion.

Besides acting as a doubly or triply bridging ligand, nitric oxide has usually been regarded as bonding to a metal in one of the following ways.

(i) By donation of one electron from an antibonding nitric oxide orbital to the metal followed by additional electron pair from $NO^+$.

(ii) By donation of two electrons to the metal from neutral NO.

(iii) By acceptance of one electron from the metal followed by electron pair donation from $NO^-$.

In these three cases nitric oxide functions as (i) a three electron donor, (ii) a two electron donor and (iii) a one electron donor.

These ideas concerning the bonding modes of NO have been regarded as valid for many years. The X-ray structural studies have, however, suggested that they must be modified. Thus, although, nitrosyl complexes may still be regarded in terms of $NO^+$ and $NO^-$, the former label is now given to those species which contain linear M-N-O bond angles, (close to $180^o$), while later is assigned to the compound with M-N-O bond angles close to $120^o$.

The ways in which $NO^+$ and $NO^-$ bind to metal to give rise to linear and bent nitrosyls, respectively, may be visualized in the following simple terms. Donation of one electron from nitric oxide to a metal results in the formation of $NO^+$; the nitrogen atom of the $NO^+$ is 'sp' hybridized, so that subsequent donation of one electron pair to the metal atom results in the formation of M-N-O bond angle of $180^o$. Alternatively donation of one electron from the metal, functioning as a Lewis base to nitric oxide, results in the generation of $NO^-$. In these species the nitrogen atom is $sp^2$ hybridised, so that donation of an electron pair by $NO^-$, results in an M-N-O bond angle of $120^o$. It must be pointed out that M-N-O bond angle in metal nitrosyls may deviate

from 180° or 120° for a number of reasons. Kettle **(102)** has suggested that because of the π-orbitals of each of the carbonyl ligands in $M(CO)_3$ system are non degenerate, the metal M, will back donate to them to different extents. Thus the M-C-O bond angles in $M(CO)_3$ system will deviate from linearity. Using the same reasoning Enemark **(103)** has shown that even in mononitrosyl species, the M-N-O bond angle will deviate **(104)** from 120°. However, deviation from the expected angles in both $NO^+$ and $NO^-$ species may occur because of packing effects in the crystal lattice.

Originally the presence of $NO^+$, NO or $NO^-$ in a compound was inferred from the position of the nitrosyl stretching in the infrared spectrum. However, the X-ray structural results have shown that the validity of assigning these labels solely on the basis of infrared spectroscopy must be seriously questioned.

The fact that nitric oxide can bond to a metal in a linear and a bent fashion means that isomerism can occur in nitrosyl complexes, because of the presence of the different bond angles in the isomers. An interesting example having both linear and bent NO group is the compound $[Co(NO)(L)_2(Cl)_2]$ (Where L = phosphine ligand). This compound is reported to have two isomers, one having linear $NO^+$ group and the other bent $NO^-$ group **(105)**.

The two bonding modes of nitric oxide not only results in different M-N-O bond angles, but also in different M-NO bond lengths. Bonding of the nitric oxide as $NO^+$ allows the metal to back donate electrons to the π*NO

orbitals causing the M-N bond to gain considerable multiple bond character. The M-N bond length will, therefore, be much shorter than that of a single M-N bond. In contrast, limited back donation from the metal will occur when $NO^-$ is bonded, so that the M-N bond length in bent nitrosyl will not be as those in linear nitrosyls.

Some of the points discussed above, as well as other effects observed in the bonding of metal nitrosyls, are best illustrated by a consideration of X-ray structural results in some cyanonitrosyl complexes (Table 1.4)

Interestingly, in all these complexes, the M-N-O angles nearly approaching to 180°, and hence the M-N-O group attachment is linear. Among the hexa–coordinated complexes, the shortest M-N bond length is found for $(FeNO)^{3+}$ and the largest has been encountered in $(CrNO)^{2+}$ group considering the first transition series.

The reported C-N distance for all these complexes is of constant value, where as for the N-O distance one can observe same variations. The expected trend is observed for the $(MoNO)^+$ and $(MoNO)^{2+}$ groups with respect to Mo-N and N-O bond distance. The insensitiveness of C-N bond distance is suggestive that the stabilization of the metal is mainly done by the nitrosyl group. Quite expectedly, vibrational spectroscopy can explain this trend along with the change in N-O bond distance. The penta-coordinated complexes containing $(FeNO)^{2+}$ group has a tetragonal pyramidal structure. The short Fe-N distance is suggestive of strong *trans* directing effect of the co-coordinated nitrosyl group, and by virtue of this effect, the compound was

isolated at low pH **(106).** The only know hepta –coordinated complex is pentagonal bipyramidal in nature and though the stability of this compound was some times thought unusual, it can now be easily explained on the basis of structural data in the bonding scheme.

*Table – 1.4*

| Compound | M-N (Å) | M-O (Å) | (M-N-O) bond angles | Coordination Number | Electron Configuration | Functional Group |
|---|---|---|---|---|---|---|
| $K_3[V(CN)_5(NO)].2H_2O$ | 1.662 | 1.294 | 171.4 | 6 | $\{VNO\}^4$ | $(VNO)^{2+}$ |
| $K_4[V(CN)_6(NO)].H_2O$ | 1.680 | 1.165 | 164.2 | 7 | $\{VNO\}^4$ | $(VNO)^{2+}$ |
| $K_3[Cr(CN)_5NO].H_2O$ | 1.990 | 1.210 | Linear | 6 | $\{CrNO\}^5$ | $(CrNO)^{2+}$ |
| $[Co(en)_3][Cr(CN)_5(NO)]$ | 1.710 | 1.210 | 176.0 | 6 | $\{CrNO\}^5$ | $(CrNO)^{2+}$ |
| $K_3[Mn(CN)_5(NO)].2H_2O$ | 1.660 | 1.210 | 174.0 | 6 | $\{MnNO\}^6$ | $(MnNO)^{2+}$ |
| $Na_2[Fe(CN)_5(NO)]$ | 1.653 | 1.124 | 175.7 | 6 | $\{FeNO\}^6$ | $(FeNO)^{3+}$ |
| $Ba[Fe(CN)_5(NO)]$ | 1.710 | 1.110 | 166.0 | 6 | $\{FeNO\}^6$ | $(FeNO)^{3+}$ |
| $(Et_4N)_2[Fe(CN)_4NO]$ | 1.669 | 1.157 | 174.7 | 5 | $\{FeNO\}^7$ | $(FeNO)^{3+}$ |
| $K_4[Mo(CN)_5(NO)]$ | 1.950 | 1.230 | Linear | 6 | $\{MoNO\}^7$ | $(MoNO)^{1+}$ |
| $(PPh_4)_3[Mo(CN)_5NO].2H_2O$ | 1.921 | 1.195 | Linear | 6 | $\{MoNO\}^5$ | $(MoNO)^{2+}$ |

**(vii) Infrared spectroscopy:**

Recent X-ray studies presented in Table 1.5 reveal the presence of linear M-NO group and thus the coordinated NO group can be regarded as $NO^+$. Thus infrared spectra of this series of complexes are widely used to obtain the information about the nitrosyl stretching frequency, i.e., the nature of ligand vibration, it is only recently that some efforts are made to locate the associated $\nu_{(M-NO)}$ and $\delta_{(M-N-O)}$ modes. Characterization of these low frequency vibrations would reflect more directly to the state of the metal-ligands bonding. The first meaningful work on this aspect was done by During etal. **(107)** on hexa–coordinated ruthenium nitrosyl halo complexes down to the frequency of 50 $cm^{-1}$. Contrary to carbonyl compounds the ν(M-NO) and δ(M-N-O) in general appear to low intensity and thus posses additional problem. Further more, dealing with the hydrated salt of cyanonitrosyl metallate, considerable difficulties are encountered in locating these vibrations because of the presence of vibrational modes due to the water and vibrations due to ν(M-NO) and δ(M-N-O). Recently to avoid the complexity due to the presence of water of crystallisation, infrared studies are made on anhydrous complexes (Table 1.5). For the relative position between the metal-nitrogen stretching and metal nitrosyl deformation mode, assignments are made from deducing the results obtained from the studies of carbonyl and cyano complexes. In metal carbonyl complexes, ν(M-CO), is lower than δ(M-C-O). The same order is usually obtained for

complexed cyanides. However, unequivocal assignments of these vibrations require $N^{15}$ and $C^{13}$ substitution data along with Raman polarization data. Some of the work on $N^{15}$substitution is done by Miki et. al. **(108)**. Using a linear three body model, they assign the higher wave number band to the M-N stretching vibration and to the lower one, M-N-O bending vibration in the lower frequency range. These assignment done on tentative basis as presented in Table 1.5. The work of Miki et. al. On cyanonitrosyl metallates are summarized in table 1.6.

Taking representative example as amine complexes, $\nu_{(M\text{-}NH3)}$, a single bond stretching frequency appears much lower **(109)** than those appeared for $\nu$(M-NO) in spite of the fact that the mass of the NO group is larger than $NH_3$ group. This represents a considerable $\pi$-back bonding in nitrosyl complexes.

## Table – 1.5

**Infrared spectral data of the cyanonitrosyl anions in the solid state**

| Compound | $\nu_{(CN)}$ | $\nu_{(NO)}$ | $\delta_{(M-N-O)}$ | $\nu_{(M-N)}$ |
|---|---|---|---|---|
| $K_3[V(CN)_5NO].2H_2O$ | 2105, 2080 | 1530 | - | - |
| $K_4[V(CN)_6NO].H_2O$ | 2095, 2100 | 1508 | 631 | 620 |
| $K_3[Cr(CN)_5NO].2H_2O$ | 2020, 2120 | 1630 | 612 | 621 |
| $K_4[Cr(CN)_5NO].2H_2O$ | 2095,2177 | 1470 | 627 | 645 |
| $K_3[Mn(CN)_5NO].2H_2O$ | 2124, 2129 | 1706 | 660 | 660 |
| $K_2[Mn(CN)_5NO]$ | 2150, 2100 | 1885 | 550 | 628 |
| $Na_2[Fe(CN)_5NO]$ | 2144, - | 1940 | 663 | 496 |
| $(Et_4N)_2[Fe(CN)_4NO]$ | 2111, 2122 | 1755 | - | - |
| $K_4[Mo(CN)_5(NO)]$ | 2120,2160 | 1450 | 589 | 604 |
| | 2097, 2080 | | | 595 |
| $(PPh_4)_3[Mo(CN)_5NO]$ | 2040, 2023 | 1580 | - | - |

## Table 1.6

### Infrared spectra of pentacyanonitrosyl complexes ($^{14}NO$ and $^{15}NO$)

| Compound | $^{14}NO$ complex | | | $^{15}NO$ complex | | |
|---|---|---|---|---|---|---|
| | $\nu_{(NO)}$ | $\nu_{(M-N)}$ | $\delta_{(M-N-O)}$ | $\nu_{(NO)}$ | $\nu_{(M-N)}$ | $\delta_{(M-N-O)}$ |
| $K_3[Cr(CN)_5NO].H_2O$ | 1643<br>1635 | 620 | 610 | 1610<br>1590 | 617 | 600 |
| $K_3[Mn(CN)_5NO].2H_2O$ | 1741<br>1733 | 663 | 663<br>653 | 1704<br>1694 | 660 | 651<br>646 |
| $K_3[Mn(CN)_5NO].2D_2O$ | 1736<br>1728 | 663 | 663<br>653 | - | - | - |
| $K_3[Mn(CN)_5NO]$ | 1711<br>1695 | 659 | 659 | 1645<br>1653 | 661 | 648 |
| $Ag_2[Mn(CN)_5NO]$ | 1888 | 628 | 628 | 1850 | 620 | 620 |

### *(viii) UV- Visible spectroscopy:*

The application of the visible spectroscopy is limited to complexes of the transition metal ions, the lanthanides and actinides. Ultraviolet spectroscopy is more universal and can be useful in structural determination of all the complexes since they all absorb in this region. In a typical transition metal complex the observed spectrum, in general, consists of a series of crystal field bands which are in the visible region and depend largely on donor atom of the ligand and on the metal ion. The crystal field transitions are of two types: the more intense spin allowed transitions and the lower intensity spin forbidden transition, which usually appear as shoulders on the spin allowed transitions. The ultraviolet spectra is complicated and consists of electronic transition between the ligand and the metal (charge transfer), and also within the ligand itself which are usually $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ transitions. The spectra of non-transition metal ion complexes usually consist only of the charge transfer and ligand transitions. The ligand transitions in all cases are characteristic of the coordinated ligand and not of the free ligand; however, the spectrum of the free ligand aids in classifying the transitions of the coordinated ligand. The intensities of the crystal field transitions never exceed a molar extinction coefficient of 500 ($\varepsilon \leq 500$), whereas the charge transfer and ligand transitions in the ultraviolet usually exceed an extinction coefficient of 500 ($\varepsilon > 500$). The spectrum of bis(phenylglycino)copper(II) is indicative of the types of transitions one may observe in a metal

complex. The transition at 16,000 $cm^{-1}$ ($\varepsilon = 65$) is a crystal field transition centered largly on the metal ion (components of $e_g \rightarrow t_{2g}$), and the transition at 36,000 $cm^{-1}$ ($\varepsilon = 3000$) are characteristic of a bound phenyl group. The transition at 39,000 $cm^{-1}$ ($\varepsilon = 6000$) has been assigned to a charge transfer apparently from the carboxyl group to the metal; the amino group-metal charge transfer and the carboxyl $\pi \rightarrow \pi^*$ transitions are at about 52,000 $cm^{-1}$. Very weak shoulders ($\varepsilon \sim 50$) in the 28,000 $cm^{-1}$ region have been assigned to the spin forbidden phenyl group transitions.

Interpretation of the results of such spectral determinations would require a complete molecular treatment. Such treatments are rare, and the methods used for such computations are only approximate in nature. The present situation is that the spectral results are used to test theories, and the correlation of the spectrum with the theory gives a greater understanding of the bonding and interactions in complexes. The visible spectra of transition metal ion complexes, however, can be well understood and described quantitatively by crystal field theory or its extension, ligand field theory.

***(ix) NMR spectroscopy :***

**Mixed-ligand complexes** - Studies of mixed-ligand complexes have cast some light on the factors which influence delocalization of electron spin from a metal onto a ligand. Eaton and Phillips found that mixed ligands complexes formed within a few minutes of adding a free aminotroponeimine to a solution of the Ni(II) complex of

another aminotroponeimine. Careful comparison enabled them to assign the contact shifts of the various protons in the mixed ligand complex. Calculation of the spin densities indicated that the values for the mixed complex are different from those for the non mixed complex, but that a reduction in spin density on one of the ligand is approximately balanced by a proportionate gain on the other ligand.

Eaton and Phillips have compared a set of variously substituted nickel(II) N-phenyl aminotroponeimineates with the N-ethyl analogs. They define a parameter

$$\zeta \equiv \frac{\Delta f_{ET} - \Delta f_{\phi}}{\frac{1}{2}(\Delta f_{ET} + \Delta f_{\phi})} = \frac{\rho_{ET} - \rho_{\phi}}{\rho_{mean}}$$

where $\Delta f_{Et}$ is the contact shift of the γ proton of the N-ethyl ligand and $\Delta f_{\Phi}$ that of the γ proton of the N-phenyl ligand in the mixed complex. They calculated $\zeta_{\gamma}$ for a whole series of mixed chelate with the various phenyl substituent and found that log $\zeta_{\gamma}$ is an excellent linear function of σ, the Hammett parameter for the phenyl substituents. Analogous results are had when the α or β proton shifts are used. These results suggest that the electron with drawing power of the substituent power of the substiuent determines the effectiveness of a particular ligand in withdrawing spin density from the metal atom.

Two theories have been offered to explain these results. Lin and Orgel have noted that in a tetrahedral mixed ligand complex the symmetry is reduced to $C_{2v}$ and the $t_2$ orbitals could be split in either of the ways shown in

the order of $b_1$and $b_2$ is not important; the authors assume for convenience that $b_2$ is below $b_1$. the important point is that $b_1$ will overlap with one ligand (in the xz plane)and $b_2$with the other (in the yz). "then In case **(A)**, since at any instant, more molecules would have the lower $b_2$ orbital doubly occupied, and the upper $b_1$ orbital singly occupied, there should be more molecules with spin delocalized on the ligand in the yz plane. The rapid inter-conversion between the planar and the tetrahedral configuration then provides a mechanism for averaging out the effect and results in an observed increase in spin densities on one ligand with a corresponding decrease on the other. In case **(B)**, in which $b_1$ and $b_2$ orbitals are similarly occupied, there should be no preferential delocalization". Lin and Orgel conclude that the uneven spin density distribution in mixed ligand complexes can probably best be explained by the fact that the ground state is doubly degenerate in symmetrical complexes, and that this degeneracy is lifted in the unsymmetrical complexes, and that this degeneracy is lifted in the unsymmetrical complexes.

More recently, however, Eaton and Phillips have presented reasons for preferring situation (B). They point out, for example, that in $C_{2v}$ the opposite situation (A) would result in two low-lying states of slightly different energy : **(1)** $b_2$ doubly opccupied, $b_1$singly occupied; and **(2)** $b_2$ singly occupied, $b_1$doubly occupied. The population of these two

states would accordingly be temperature dependent, as would the ratio of spin delocalized onto each of the two different ligands. Their calculations show that the change in ratio should be readily observable in the temperature show that the change in ratio should be readily observable in the temperature range available for PMR measurements. Over a range of 120° they found that the ratio of spin delocalized, instead of increasing with decrease in temperature, actually decreased. In place of Lin and Orgel's explanation they offer an alternative one based on Jaffe's idea of competitive $\pi$ bonding in tetrahedral complexes. They assume situation (B). With $b_1$ and $b_2$ levels equally occupied. Each of these can form a $\pi$ bond with one ligand, but the extent of the $\pi$ bond formation and consequent spin density transfer to each ligand will depend on the nature of the ligand. In general there will be a competition between the two ligands, and the molecule will assume that orientation which allows maximum orbital overlap and $\pi$ bond formation. They note also that this interpretation fits nicely with the excellent correlation found between the Hammett $\sigma$ parameter and their own $\zeta$ parameter.

Proton NMR spectroscopy has been used to investigate paramagnetic complexes of low-valent transition metal ions because the contact shifts provide information on the degree of covalency of the metal-ligand bond. The low spin complexes $[Cr(phen)_3]Cl_2$ and $[Cr(bipy)_3]Cl_2$, their methyl substituted derivatives, have been

extensively investigated **(39, 41, 42).** Narrow, well-resolved $^1H$ NMR spectra have been obtained from $[Cr(R_2phen)_3]^{2+}$ (R=H; $R_2$=4, 7- and 5,6-dimethyl) and $[Cr(R_2bipy)_3]^{2+}$ (R=H; $R_2$=4, 4'-dimethyl) and the shifts result from both L→M σ and M→L π charge transfer. The π bonding is not obvious in the tris chelates with symmetric ligands owing to near cancellation of two contributions of opposite sign **(41).**The relative π-acceptor abilities of the differently substituted ligands, and the orbital ground state of the complexes were elucidated only after some mixed-ligand chelates (Obtained in solution only) had been investigated. The M→L delocalized π spin density is centred predominantly at the 4, 7 positions of phen or 4, 4' positions in bipy. This facilitates the reducing ability of these chelates and is believed **(42)** to be consistent with the stereoselective outer sphere reduction of $[Co(phen)_3]^{3+}$ by $[Co(phen)_3]^{3+}$: it is found that (+)-$[Co(phen)_3]^{3+}$ yields (–)-$[Co(phen)_3]^{3+}$ as the main product on reduction with racemic $[Co(phen)_3]^{3+}$ **(43).** Anamalously broadened methyl resonances are ascribed to the solvent(water) complex interaction at the 4, 7 positions which involve hydrogen bonding to pockets of electron density on the ligand assisted by the π bonding. From spectral changes it was suggested **(35)** that bipy separated from $[Co(bipy)_3]X_2$ (X = Cl, Br, I) in ethanol, but there are no NMR signals of free ligand from solutions of these salts in $d_4$-MeOH unless some is added

Studies of mixed-ligand complex have cast some light in the factors which influence delocalization of electron spin. The principal difficulty in the investigation of paramagnetic organaometallics lies in their NMR spectra. The presence of unpaired electrons in the same molecule results in large isotopic shift (upto several hundred ppm) and severely broadened resonances =, which usually obscure any nuclear spin-spin coupling and make integration of signals difficult. Nuclei bonded directly to the metal (e.g. hydrides), or even protons attached to the carbon atoms directly bonded to Cr(III) (e.g. methyl groups) are typically unobservable. The magnitude of these effects depends on the number of unpaired electrons and the electron spin relaxation time, varying with the metal, formal oxidation state and the coordination environment. In effect, there exists no generally applicable empirical relationship between chemical shift and chemical environment, and the line broadening can make signals of low intensity all but undetectable. That said, NMR spectra of paramagnetic compounds are easily acquired, simply by increasing the sweep width of the FT NMR spectrometer and rapidly pulsing away.

When the line broadening becomes a serious obstacles one can take advantage of a phenomenon that results in narrower lines. Specifically, substitution of $^{1}H$ atoms with the $^{2}H$ isotope coupled with $^{2}H$ NMR spectroscopy results in spectral lines that are up to 40 times narrower than those of corresponding $^{1}H$ NMR spectra, due to slower nuclear

relaxation of the $^{2}H$ nuclei in paramagnetic compounds. One of the apparent disadvantages of this technique would seem to be the need for the preparation of selectively deuterium labeled compounds. However, with modern FT NMR equipment, the natural abundance of deuterium can be sufficient to take advantage of the line narrowing effect by recording $^{2}H$ NMR spectra of unlabelled compounds.

Isotope exchange experiments also revealed another peculiarity of the NMR spectra of the paramagnetic compounds, namely the observation of extremely large isotope effects on chemical shifts (we have coined the acronym PIECS, i.e. Paramagnetic Isotope effect on chemical shift, for this phenomenon). A particularly interesting case of this was observed in H/D exchange reactions of the $[Cp_4''Cr_4(\mu_3\text{-}H)_4]$, yielding mixtures of isotopomers of the constitution $[Cp_4''Cr_4(\mu_3\text{-}H)_n(\mu_3\text{-}D)_{4\text{-}n}]$. The $^{13}C$ NMR resonances of cyclopentadienyl ring exhibited shifts of up to 3 ppm per incremental H/D substitution. Indeed, this phenomenon was used unambiguously 'count' the number of hydrides present in the cluster and to reveal a dynamic process that exchanges them rapidly on the NMR time scale.

### *(x) Redox properties:*

The one electron reduction of $[Cr(CN)_5(NO)]^{3-}$, was first demonstrated by Wilkinson and co-workers **(28)**. They used the polarographic method of reduction and could not be able to isolate the oxidized product at that time. Few years

later, Griffith using same method have been able to isolate, $[Cr(CN)_5(NO)]^{4-}$. Cotton and co-workers have isolated the one electron oxidized product of $[Mn(CN)_5(NO)]^{3-}$ using bromine or nitric acid as oxidizing agent **(41)**. The extra stability achieved by coordinated nitric oxide for a particular metal can be seen from the isoelectronic redox system for the manganese complex (Table 1.7).

The nitroprusside analogue of Rhenium shows reduction, which is a reversible one, as may be expressed:

$$[Re(CN)_5(NO)]^{2-} + e^- \rightleftharpoons [Re(CN)_5(NO)]^{3-}$$

Jacab etal. studied quantitatively one electron oxidation of $[Re(CN)_5(NO)]^{4-}$, which is a reversible one **(111)**. However, several attempts to isolate the oxidized product failed, and it is only recently $[Mo(CN)_5(NO)]^{3-}$ has been synthesized and characterized. A comparative study of the electrochemistry of $[Fe(CN)_5(NO)]^{2-}$ at $NO^+$ itself has been made **(112)**. The nitrosonium ion shows three reduction waves and these have been interpreted as the formation of NO in the first stage, which then dimerized and reduced to $N_2O_2^{2-}$ in the second part of reaction.

## *Table 1.7*

### *Standard electrode Potential*

| Couple | $E_0(V)$ |
|---|---|
| $[Cr(CN)_5NO]^{3-}$ / $[Cr(CN)_5NO]^{4-}$ | -1.146 |
| $[Mn(CN)_6]^{4-}$ / $[Mn(CN)_6]^{5-}$ | -1.06 |
| $[Mn(CN)_5]^{2-}$ / $[Mn(CN)_5NO]^{3-}$ | +0.597 |

The third phase corresponds to three electrons reduction of NO into $NH_2OH$. The $[Fe(CN)_5(NO)]^{2-}$ anion first undergoes reduction to $[Fe(CN)_5(NO)]^{3-}$, which undergoes either protonation and reduction via second wave or formation of the complex $[Fe(CN)_5(NH_2OH)]^{3-}$ which has been isolated by the used conventional chemical method **(42)**. This isolation demands a reinterpretation of the earlier electro-chemical studies on nitroprusside anion **(113, 114)**.

### *(xi) X-ray photoelectron spectroscopy:*

The X-ray photoelectron spectra may be used for studying the chemical bonds in the co-ordination compounds owing to the fact that the binding energy $E_b$ of the inner shell electrons depends upon the effective charge q. The binding energy of electrons of the atoms in chemical compounds are usually characterized by the changes (Shifts , $\Delta E$) of these energies in the compound studied compared to the energies in the reference compound. Under these conditions, a positive shift corresponds to the positive effective charge of

the atom in the compound under study and the negative shift corresponds to the negative effective charge. The direct correlation of the atomic charge and the shift is a simplified procedure.

The effective charge of the NO group has been discussed for the last many years **(115)**. This anomaly in this field is due to the fact that the actual electron density distribution is rather for from both limiting descriptions $NO^+$ and $NO^-$ , and the absence of the clear cut physical concept of the oxidation state in this case may give rise to apparent contradictions. The oxidation state of the metal atom for the sign of the charge of the NO group are determined by evaluating how close certain physico-chemical characteristics of the nitrosyl compounds are to those of the above limiting cases. These characteristics are sensitive to various aspects of the electron density distribution so that the boundary between $NO^-$ and $NO^+$ cases depends on the characteristics considered and the problem concerns only the measurement of a physically observed parameter. Thus the closest, correspondence to the classical chemical concepts, for example, the oxidation state of a metal atom may be obtained with such observable parameters, which describe the extent to which the electron density is drawn away from an atom or a group.

The $N_{1S}$ value for $NO^+$ in NOCl is about 409 eV and 406 eV for the neutral molecule. The extrapolation of the data for $NO^+$ and $NO^-$ yields the range of $N_{1S}$ value for $NO^-$ in vicinity of 402 eV.

Flokesson **(116)** started a systematic photoelectron spectral study of cyanonitrosyl complexes. The results are tabulated in Table 1.8. The $N_{1S}$ binding energies for the cyanide group in this series reflect the observation made by ν (CN) in infrared spectroscopy as discussed earlier. Interestingly, most of the $N_{1S}$ binding energy for the nitrosyl groups falls below 402 eV and hence can be treated as containing the nitrosyl group $NO^-$. According to the arguments put before, the nitrosyl group in nitroprusside can be said to contain a formally positive charged 'N' that is, $NO^+$. However, these data are insufficient in the sense that they do not say any thing about the bonding energies of the metal electrons. A comparison of a series of a particular metal in its complexes containing different oxidation states having the same coordination number would have been more useful in assessing the charge distribution. Furthermore, the ESCA data of a cyanonitrosyl metallate ions in its consecutive reduced or oxidized state as in some cases it is formed, would supplement the study. The first point of the above use has been studied by Nefedov **(117)**, where he compared the $Fe_{2p}3/2$ energies in $Na_2[Fe(CN)_5(NO)]$, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. These data are presented in Table 1.9, along with the data for $Fe(n^5\text{-}C_5H_5)_2$. The trend in 2p3/2 according to the given Table suggests that iron in nitroprusside is in high oxidized state compared to even that in $K_3[Fe(CN)_6]$, meaning thereby that the formal oxidation state of Fe in nitroprusside would be IV. Furthermore, in the absolute sense the $N_{1S}$ binding energy for NO is even lower for the

neutral NO molecule, suggesting that the coordinated nitric oxide even in nitroprusside should be treated as $NO^-$.

***Table 1.8***

***ESCA data of the cyanonitrosyl complexes***

| *Compound* | $E_bN_{1S}(NO)$ *(eV)* | $E_bN_{1S}(NO)$ *(eV)* | *Electron configuration* $\{MNO\}^n$ |
|---|---|---|---|
| $[V(CN)_5(NO)]^{3-}$ | 400.00 | 398.8 | $\{VNO\}^4$ |
| $[Cr(CN)_2(NO)]^{3-}$ | 401.4 | 399.0 | $\{CrNO\}^5$ |
| $[Mn(CN)_5(NO)]^{3-}$ | 401.6 | 398.3 | $\{MnNO\}^6$ |
| $[Mn(CN)_5(NO)]^{3-}$ | 402.1 | 298.3 | $\{MnNO\}^5$ |
| $[Fe(CN)_5(NO)]^{2-}$ | 403.0 | 398.7 | $\{FeNO\}^6$ |
| $[Mo(CN)_5(NO)]^{4-}$ | 401.1 | 398.8 | $\{MoNO\}^6$ |
| $[Mo(CN)_5(NO)]^{3-}$ | 400.1 | 398.8 | $\{MoNO\}^5$ |

## *Table 1.9*

### *Binding energies (eV) of some iron complexes*

| Compound | Fe $P_{3/2}$ (eV) | $N_{1S}$(NO) (eV) |
|---|---|---|
| $Fe(n^5\text{-}C_5H_5)_2$ | 708.0 | |
| $K_4[Fe(CN)_6]$ | 708.8 | |
| $K_3[Fe(CN)_6]$ | 710.3 | |
| $[Fe(CN)_5(NO)]^{2-}$ | 403.0 | 402.6 |
| $Na_2[Fe(CN)_5NO]$ | 711.0 | 403.6 |

Attempts have been made by Sarkar and Muller **(118)** to observe the changes appear in the two adjacent reduced and oxidized species of nitrosyl complexes of Molybdenum. This has been done on the ground to observe the changes occurred in the $3d_{3/2}$ and $3d_{5/2}$ binding energies of coordinated NO. For a redox reaction,

$$(MoNO)^{n-} \xrightarrow{e^-} \{MoNO\}^{n-1} \text{ (n = number of 'd' electrons)}$$

the overall electronic distribution in MoNO moiety will change. The release of an electron may takes place (i) from the molybdenum ion, (ii) from the nitrosyl ligand (iii) on inseparable withdrawn of an electron from both the centers that is from MNO group. From the crystallographic data of $K_4[Mo(CN)_5(NO)]$ and $(PPh_4)_3[Mo(CN)_5NO].\ 2H_2O$ (vide Table 1.4 ), it is known that the Mo-N bond is the oxidized species $\{MoNO\}^5$ is shorter than that of $\{MoNO\}^6$ group containing compound,. This shorting is due to a stronger Mo-NO attachment in the former species than the later. The stronger attachment can be only visualized by the increase back donation from Mo $\rightarrow$ NO, leading thereby accumulation of more electron density on NO>. The observed trend present in Table 1.8, It is interesting to note that there is overall no electronic change of the cyanide group present as co-ligand in both the complexes.

X-ray photoelectron spectrum of $[Cr(NO)(acac)_2]$ in the binding energy range (365-415 eV) has been studied by Maurya et. al. They observed the $N_{1S}$ binding energy of the coordinated NO group is 401.8 eV which is comparable to the reported for potassium pentacyanonitrosylchromate(I).

The slight increase in the value may be due to the neutral nature of the complex. It appears, therefore, that NO in this compound is present as $NO^+$ just by comparing the $N_{1S}$ value of $K_3[Cr(CN)_5NO]$, where coordination of nitric oxide as $NO^+$ is already established by X-ray studies **(119)**.

## 1.4 REACTIVITY OF COORDINATED NITRIC OXIDE

The study of the reactivity of the metal nitrosyls compare to the metal carbonyl complexes is rare. This is due to the fact that the coordinated nitric oxide is very firmly bound with the metal and the ligand displacement reactions are not found so commonly as these happen with the metal carbonyls. Due to the enormous studies on the metal carbonyls having industrial significance in recent years, many facts concerning the reactivity of nitrosyl complexes have emerged. Two things are of prime importance in these studies. The first one is to deal with the environment pollution caused by nitric oxide and the second one is the development of newer catalytic system of industrial applicability.

The reactivity of coordinated nitric oxide falls under the following types:

### (i) Reduction and Disproportionation:

One electron reduction of $[Fe(CN)_5(NO)]^{2-}$ gives brown, $[Fe(CN)_5(NO)]^{3-}$, which ultimately affords $[Fe(CN)_4NO]^{2-}$. The reduction of $\{Fe^{III}NO\}^6$ moiety has been explained to produced via $\{Fe^{II}NO\}^7$ as intermediate in the brown complex, which ultimately changes to $\{Fe^{I}NO\}^7$

**(120)**. The reduction commonly occurs at the metal centre **(121)** and there are some examples, where reduction takes place on the co-ligand sites **(122)**. In non-protic media multi-electron reduction of $[Fe(CN)_5(NO)]^{2-}$ gives $[Fe(CN)_5(NO)]^{3-}$, $[Fe(CN)_4NO]^{2-}$, $[Fe(CN)_4NO]^{3-}$, $[Fe(CN)_3NO]^{3-}$, $[Fe(CN)_3NO]^{4-}$.

Using dispersed platinum metal oxide or metal gauge as catalysts, the reduction of NO to either ammonia or dinitrogen has been achieved. This heterogeneous reduction is used in treatment of automobile exhaust gas pollution **(123)**. Using some sodium and Iridium nitrosyl and carbonyl complexes, mixtures of NO and CO may be disproportionated into $N_2O$ and $CO_2$ **(124, 125)**.

**Nucleophilic attack:**

This is most well known reactivity of the nitrosyl complexes, which can classically exemplified by the following reaction **(126)**.

$$[Fe(CN)_5(NO)]^{2-} + 2OH^- \longrightarrow [Fe(CN)_5NO_2]^{4-} + H_2O$$

This reaction has an equilibrium constant of $1.5 \times 10^6$, which may be compared to the value of $2.3 \times 10^{23}$ for the parent reaction:

$$NO^+ + 2OH^- \longrightarrow NO_2^- + H_2O$$

Clearly, coordinated $NO^+$ in $[Fe(CN)_5(NO)]^{2-}$ is a much weaker electrophile than free $NO^+$. The corresponding ruthenium and osmium analogues behave similarly **(127, 128)**.

A number of reactions are known, where a lot of nucleophiles have been used instead of $OH^-$ and the general reactivity is of the same nature as given below **(129, 130)**:

$$PhNH_2 + NO^+ \longrightarrow PhN_2^+ + H_2O$$

$$[Ru(Cl)(bipy)_2(NO)]^{2+} + PhNH_2 \longrightarrow [Ru(Cl)(bipy)_2(N_2Ph)]^{2+} + H_2O$$

$$[Ru(NH_3)_5NO]^{3+} + NH_2OH \longrightarrow [Ru(NH_3)_5N_2O]^{2+} + H_3O^+$$

The formation of novel intermediate entities using this type of nucleophilic attack has been demonstrated by Bottomley and co-workers **(132, 133)** which is shown below:

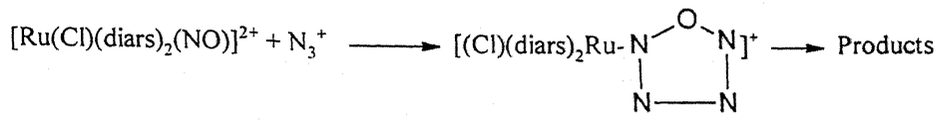
$$[Ru(NH_3)_5NO]^{3+} + OH^- \longrightarrow [Ru(NH_2)(NH_3)_4NO]^{2+} + H_2O$$

$$[Ru(NH_3)_5NO]^{3+} + [Ru(NH_2)(NH_3)_4NO]^{2+} \longrightarrow cis\text{-}[RuOH(NH_3)_4(NO)]^{2+} + [Ru(NH_3)_5N_2]^{2+} + H^+$$

When $N_3^-$ is used, the reaction may be depicted as below **(126)**:

$$[Ru(Cl)(dipy)_2NO]^{2+} + N_3^- \longrightarrow [Ru(Cl)(dipy)_2(S)]^+ + N_2 + H_2O$$

Where 'S' indicates a solvent molecule like $H_2O$, MeCN, MeOH or $Me_2CO$. The formation of the labile $[RuCl(dipy)_2S]^+$ has been exploited for the preparation of $[RuCl(dipy)_2X]^{n+}$ complexes where X is a monodentate ligand **(133-137)**. In the case of reaction between $[Ru(Cl)(diars)_2NO]^{2+}$ and $N_3^-$, isotopic labeling gave evidence for attack of $N_3^-$, at coordinated NO with formation of a cyclic $N_4O$ intermediate **(138)**.



### *(ii) Electrophilic attack:*

By the mode of attack, it is evident that the activity of the coordinated No would be associated just in the opposite direction as encountered in nucleophilic attack. This attack is therefore, associated with the nitrosyl complexes where M-N-O group is bent or in other words the nitrosyl group contains formally $NO^-$. The extent of protonation in this group depends on the formal oxidation state of the metal and the trends observed are shown below:

$$[Os(Cl)(CO)(NO)(PPh_3)_2] + HCl \longrightarrow [Os(Cl)_2(CO)(NHO)(PPh_3)_2]$$

$$[Os(NO)_2(PPh_3)_2] + 2HCl \longrightarrow [Os(Cl)_2(NHOH)(NO)(PPh_3)_2]$$

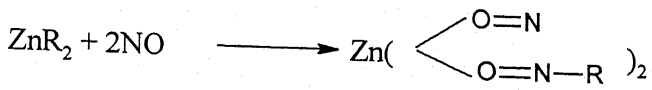
$$[Ir(NO)(PPh_3)_2] + 3HCl \longrightarrow [Ir(Cl)_3(NH_2OH)(NO)(PPh_3)_2]$$

The above cited nucleophilic and electrophilic attacks suggest a broad division like the linear M-N-O group containing $NO^+$ should be unstable in alkaline medium, whereas the bent M-N-O group containing $NO^-$ should be unstable in acidic medium. From the synthetic point of view, the cyanonitrosyl complexes prepared in acidic medium should behave like nitroprusside anion, and which is in-fact found to be true. Contrary to this the cyanonitrosyl prepared using alkaline hydroxylamine method, though some what

using alkaline hydroxylamine method, though some what unstable in acidic medium, do not contain bent nitrosyl group (vide supra). Nevertheless, it has been demonstrated that complexes containing the same moiety can be isolated in alkaline as well as acidic media. This once more reflects our lack of understanding about the variation of actual electron density in the linear M-N-O group. Attempts **(145-147)** are being made to answer this uncertainty. However, a complete answer is still awaited.

***(iii) Some other reactions of interest:***

It is known that NO can be inserted into M-C bond. A representative scheme is –



Other transition metals have been used similarly **(139).**

Recently it has been demonstrated that though a coordinated nitrosyl remains intact, yet it can activate the metal centre so that dimethylformamide can be bonded to the metal as carbamide moiety **(140).**

The use of dinitrosyl molybdenum derivatives have been made for the olefin metathesis reaction involving the intermolecular exchange of alkylidine units between alkene via cleavage of C=C bond as co-catalyst **(141, 142).**

A very useful synthetic procedure has been observed where coordinated NO may be transferred to the other metal**(143)**, for example,

## 1.5 SCOPE OF THE WORK

The synthesis, bonding and reactivity of the nitrosyl complexes are complexed and varied. Mono nitrosyl complexes containing $\{MNO\}^n$ group having cyanide as co-ligand are comparatively less explored regarding substitution reactions keeping the (MNO) moiety intact. As described in the preceding part of the chapter, a fairly balanced physico-chemical studied along-with X-ray structural data are now available, but for accounting the reactivity of these complexes, there is definitely paucity of data compared to other nitrosyl derivatives. Among the cyanonitrosyl complexes, it is only nitroprusside anion which received much attention in all respects.

The comparative rate of attention regarding substitution reaction in nitrosyl complexes containing cyano group as co-ligand as well as without cyano group are summarized in Table 1.10.

An examination of table shows that except for $d^6$-configuration the cyanonitrosyl chemistry of other electronic configuration is very poorly studied with respect to their reactivity and substitution reactions as a more general outlook for the fast development of the nitrosyl chemistry containing electronic configuration $d^6$ and more lies on the theoretical interpretation regarding the electronic distribution in the (MNO) moiety. This is due to the fact that on populating electrons in the antibonding orbital (vide supra) cause destabilization of the bonding between metal and

nitrosyl centres enhancing thereby the reactivity of the co-ordinated NO group. Keeping these possibilities in mind different substitution reactions were carried out by changing the substituent, to get slight modification of the electronic distribution in the (MNO) group depending on the nature of donor and π-acceptor capabilities of the substituent ligands. These maneuvering sometimes lead to restrict the uncontrollable reactivity of the co-ordinated NO group or the reverse.

From the view points discussed above, it is obvious that the nitrosyl complexes containing $d^6$ electronic configuration do not feel any destabilization because the highest occupied orbital is non-bonding. However, maximum studies on this electronic configuration were made on two grounds. Firstly, from the theoretical consideration this electronic configuration can not act some sort of base line from which a comparison can be made for the others containing more number of 'd' electrons. Secondly, it is merely coincidental that nitrosyl complexes of this configuration existed long back (by the celebrated example of nitroprusside and easily recognized class of nitrosyl Ruthenium(III) compounds) before the bonding scheme were devised, which resulted the development of nitrosyl chemistry on this electronic configuration.

The existing theories on different nitrosyl complexes do not suggest anything of the $d^4$ and $d^5$ electronic configuration. This is partly responsible for the paucity of

nitrosyl complexes with these configurations and so when they are recently being explored, gave interesting results. As it is often discussed earlier that in cyanonitrosyl complexes stabilization reset mainly on the nitrosyl group which indicates the cyanide co-ligand should be mobile in nature and can be displaced by other ligands of interest. A judicious choice of different ligands containing different donor sites would be of much preparative interest and with their nature of perturbation of the (MNO) moiety one can think a bit differently to see whether a particular condition for the introduction of nitrosyl group is very much specific or not.

In the preparative sense, only very little nitrosyl complexes of chromium(I) are reported. As acid hydrolysis of $[CrNO(CN)_5]^{3-}$ **(94),** has been followed using ESR technique and also by polarigraphy, it would be of interest to see whether the different equation products can be isolated using different nitrogen donors. This type of nitrosyl derivatives are mostly known with ruthenium complexes containing $d^6$ configuration. As $d^5$ chromium(I) and $d^6$ ruthenium(II) complexes contain the highest populated orbital of non-bonding nature, a comparative chemistry in light of bonding theories would be interesting.

From Table 1.10, it is evident that complexes containing $(CrNO)^{2+}$ moiety are mostly cationic type. Anionic complexes are restricted to only on the preparation of $[CrNO(CN)_5]^{3-}$. It would be of interest to see whether other anions of different complexing abilities using ESR

technique. Besides, non-electrolytic complexes containing $(CrNO)^{2+}$ moiety is very little known. An attempt in this synthetic approach would make the scope more relevant.

The complexes thus synthesized would require an attention of reactivities, which can be dealth using different physico-chemical techniques. Thus a correlation can be made on the changes noticed with the help of existing theories in hand.

## *Table 1.10*

| *Electronic configuration {MNO}$^n$ (where n is number of d electrons* | *Coordination Number* | *Relative chemistry with representative known species* |
|---|---|---|
| With 'CN' group | 6 and 7 | Poorly known, $[V(CN)_5(NO)]^{3-}$ $[V(CN)_6(NO)]^{4-}$ |
| $d^4$ | | |
| Without 'CN' group | 5, 6 and 7 | Fairly known, $[V(DTC)_2NO]$, $[MoCl_4(NO)]^-$ $[MoCl_4(NO)]^{2-}$ and $[Mo(DTC)_3(NO)]$ |
| With 'CN' group | 6 | Poorly known, $[Cr(NO)_5(NO)]^{3-}$ |
| $d^5$ | | |
| Without 'CN' group | 6 | Moderately known, $[Cr\ (NO)\ L_5]^{2+}$ |
| With 'CN' group | 6 | Well known, $[Fe(CN)_5(NO)]^{2-}$ |
| $d^6$ | | |
| Without 'CN' group | 6 | Well known, $[RuX^5(NO)]^{2-}$ |
| With 'CN' group | 5 and 6 | Poorly known, $[Fe(CN)_4(NO)]^{2-}$ and $[Fe(CN)_5(NO)]^{3-}$ |
| $d^7$ | | |
| Without 'CN' group | 6 | Moderately known, $[Fe\ L_5\ (NO)]^{2+}$ |
| With 'CN' group | 6 | Poorly known, $[Pt(CN)_5(NO)]^{2-}$ |
| $d^8$ | | |
| Without 'CN' group | 5 and 6 | Widely known, $[Co(NH)_3(NO)]^{2+}$, $[Mn(CO)_4(NO)]$, $[MnL_2(NO)_2X]$ and |

Continue Table 1.10

| | | |
|---|---|---|
| | | $[Cr(NO)_5(NO)]^3$<br>$[Co(NO)L_2X_2]$ |
| With 'CN' group | | Unknown |
| | $d^9$ | |
| Without 'CN' group | 4 | Fairly known,<br>$[Fe(NO)_2X_2]$ and<br>$[Co(NO)(L)(SR)_2]$ |
| With 'CN' group | 4 | Poorly known,<br>$K_2[Ni(CN)_3(NO)]$ |
| | $d^{10}$ | |
| Without 'CN' group | 4 | Most widely known,<br>$[Mn(NO)_3L]$,<br>$[Fe(NO)_2(CO)L]$,<br>$[Fe(NO)_2L_2]$,<br>$[Co(NO)(CO)_2L]$,<br>$[Ni(NO)X]_n$, $[Ni(CO)L_2X]$,<br>and $[Fe(NO)_2(RNC)_2]$ |

## REFERENCES


1. N. V. Sidwick, "The chemical elements and their compounds" Vol. II, P- 344, Oxford at the Calendron Press (1850).

1a G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.),'Comprehensive Organometallic Chemistry', Pergamon, Oxford 1982, Vol. 3.

2. J.G. Swinehart, Coord. Chem. Rev., 2, 385 (1967).

3. K.G. Calton, Coord. Chem. Rev., 2, 318 (1967).

4. J.A. McCleverty, Chem. Rev., 79, 53 (1974).

5. B.F.G. Johnson and J.A. McCleverty, Progr.Inorg.Chem., 7, 277 (1966).

6. W.P.Griffith, Adv. Organometallic Chem., 7, 211 (1968).

7. J.Lewis, R.J. Irwing and G. Willkinson, J. Inorg. Nucl. Chem., 7, 32 (1958).

8. B.F. Hoskins, F. D. Whillens, D.H. Dale and D.C. Hodgkin, J. Chem. Soc. Chem. Comm., 69 (1969).

9. P. Gans, J. Chem. Soc. Chem. Comm., 144 (1965).

10. L.Y.Y. Chan and F.W.B. Elnstein, Acta Cryst., 26B, 1899 (1970).

11. R.C. Eider, Inorg. Chem., 13, 1037 (1974).

12. W. P. Griffith and G. Willkinson, J. Inorg. Nucl. Chem., 7, 285 (1958).

13. A. Muller, P. Werle, E. Diemann and P.J. Aymonino, J. Ber., 105, 2419 (1972).

14. G.B. Richael Drew and F. Chrstopher, Pygall, Acta. Cryst. Sect. B., 33 (9), 2838 (1977).

15. R. Calton, R.D. Peacock and G. Willkinson, J. Chem. Soc., 1374 (1960).

16. H. Behrens, E. Lindncer and H. Schindler, Z. Anorg. Chem., 365, 119 (1969).

17. W. Hieber and H. Fuhrling, Z. Anorg. Chem., 373, 48 (1970).

18. H. Behrens, E, Lindner and H. Schindler, Chem. Ber., 99, 2399 (1966).

19. M. A. Zolfigol et al., Tetrahedron, 57, 1627, (2001)

20. Suzuki, N.; Higuchi, T,; Urano, Y.; Kikuchi, K.; Uchida, T.; Mukai, M.; Kitagawa, T.; Nagano, T. J. Am. Chem. Soc., 122, 12059 (2000).

21. Alicja Frank, Grazyna Stochel, Noriyuki Sujuki, Tsunehiko Higuchi, Kimiko Okuzono and Rudi Van Eldic, J. Am. Chem. Soc., 127, 5360 (2005).

22. R. C. Maurya and R. Verma, Indian J. of Chem., 36A, 437, (1997).

23. S. Sarkar, R. C. Maurya, S.C. Chaurasia, and R. Srivastava, Transition Met. Chem., 1, 49 (1976).

24. R. C. Maurya, Indian J. of Chem., 22A, 529 (1983).

25. R. Bhattacharya and P.S. Roy, Transition Met. Chem., 9, 280 (1984).

26. W. Hieber, R. Nast and G. Gahring, Z. Anorg. Allgem. Chem., 256, 169 (1948).

27. K. Vonder Heide and A. Hofmann, Z. Anorg. Allgem. Chem., 12, 277 (1896).

28. W. P. Griffith, J. Lewis and G. Willkinson, J. Chem. Soc., 872 (1959).

29. W. P. Griffith, J. Lewis and G. Willkinson, J. Chem. Soc., 1632 (1959).

30. R. Bhattacharya, G.P. Bhattacharjee and A.M. Saha, Polyhedron, 4, 583 (1985).

31. R. Nast, W. Hieber, and E. Proeschal, Z. Anorg. Allgem. Chem., 226, 145 (1948).

32. L. Malaesta and A. Sacco, Z. Anorg. Allgem. Chem., 274, 341 (1953).

33. A. Muller, P. Werle, E. Diemann and P.J. Aymonino, Chem. Ber., 105, 2419 (1972).

34. W. P. Griffith, J. Chem. Soc., 3286 (1963).

35. C. M. Lukehart and J. N. Troup, Inorg. Chim. Acta., 22, 81 (1977).

36. R.F. Riley and L. HO, J. Inorg. Nucl. Chem., 24, 112 (1962).

37. L. Playfair, Proc. Roy. Soc. (London), 5, 846 (1849).

38. E.J. Beran and A. Muller, 2, Anorg. Allgem. Chem., 370, 283 (1969).

39. G. N. La Mar and G. R. Van Hecke, J. Am. Chem. Soc., 91, 3442, (1969).

39a. 35. A. Earnshaw, L. F. Larkworthy, K. C. Patel and B. J. Tucker, J. Chem. Soc., Dalton Trans., 2209, (1977).

B.K. Sen, N.N. Ghosh and P.B. Sarkar, J. Indian Chem. Soc. 40, 707 (1963).

40. S. Sarkar and A. Muller, Z. Naturfurschung, 33B, 1053 (1978).

40a. G. N. La Mar, J. Am. Chem. Soc., 94, 9055, (1972).

41. F.A. Cotton, R.R. Monchamp, R.J.M. Henry and R.C. Young, J. Inorg. Nucl. Chem., 10, 55 (1974).

41a. G. N. La Mar and G. R. Van Hecke, Inorg. Chem., 12, 1767, (1973).

42. J. Schimdt, H. Ruhr, W.L. Dorn and J. Kopf, Inorg. Nucl. Chem. Lett., 10, 55 (1974).

42a. J. H. Sutter and J. B. Hunt, J. Am. Chem. Soc., 91, 3107, (1969).

43. R. Nast and J. Schimdt, Angew. Chem. (Internat. Edn.), 8, 383 (1969).

44. J. Schimdt, H. Ruhr, W.L. Dorn and J. Kopf, Inorg. Nucl. Chem. Lett., 10, 55 (1974).

45. H. Behrens, E. Lindncer and H. Schindler, Z. Anorg. Chem., 365, 119 (1969).

46. J. Ellermann, H. Behrens, E, Lindncer and H. dobrzanski and F. Poresch, Z. Anorg. Allgem. Chem., 361, 306 (1968).

47. P. T. Manoharan and W.C. Hamilton, Inorg. Chem., 2, 1043 (1966).

48. I. Burnel and S.E. Harrison, J. Chem. Phys., 34,

102 (1971).

49. D.A.C. McNeil, J.B. Rayner and M.C.R. Symons, Proc. Roy. Soc. (London), 364 (1964).

50. D.A.C. McNeil, J.B. Rayner and M.C.R. Symons, J. Chem. Soc., 410 (1965).

51. J.J. Fortemen and R.C. Hayes, J. Chem. Phys., 43, 15 (1965).

52. H.A. Kuska and M.T. Rogers, J. Chem. Phys., 42, 3034 (1965).

53. B.A. Goodman, J.B. Rayner and M.C.R. Symons, J. Chem. Soc., A. 994 (1966).

54. I. Burnel, S.D. Robinson, L.S. Meriwether and G. Willkinson, J. Chem. Soc. Chem. Comm., 571 (1965).

55. G.R. McCarney and J. Pearlman, J. Chem. Phys., 46, 4992 (1967).

56. P. T. Manoharan and H.B. Grey, J. Chem. Soc. Chem. Comm., 324 (1965).

57. I. Burnel, S.E. Harrison, J. Chem. Phys., 34, 102 (1971); 38, 258 (1963);

58. I. Burnel, S.D. Robinson, L.S. Meriwether and G. Willkinson, J. Chem. Soc. Chem. Comm., 571 (1965).

59. J. Burgess, B.A. Goodman and J.B. Rayner, J. Chem. Soc., A, 501 (1968).

60. J. Danon, H. Panepucci and A.A. Misetich, J. Chem. Phys., 44, 4154 (1968).

61. J.J. Fortemen and R.C. Hayes, J. Chem. Phys., 43, 15 (1965).

62. B.A. Goodman, J.B. Rayner and M.C.R. Symons, J. Chem. Soc., A. 1973 (1968).

63. J.B. Spancer and R.J. Myers, J. Am. Chem. Soc., 86, 522 (1964).

64. L.S. Meriwether, S.D. Robinson and G. Willkinson, J. Chem. Soc. A. 1488 (1966).

65. J. Burgess, B.A. Goodman and J.B. Rayner, J. Chem. Soc., A, 501 (1968).

66. J. Danon, R.P.A. Muniz and H. Panepucci, J. Chem. Phys., 41, 363 (1984).

67. P. T. Manoharan and H.B. Grey, J. Chem. Soc. Chem. Comm., 324 (1965).

68. D.A.C. McNeil, J.B. Rayner and M.C.R. Symons, J. Chem. Soc., 410 (1965).

69. D. Vanormondt and J. Thalammerm, Phy. Letters, 14, 169 (1965).

70. P. T. Manoharan and H.B. Grey, Inorg. Chem., 5, 823 (1966).

71. P. T. Manoharan, H.A. Kuska and M.T. Rogers, J. Am. Chem. Soc., 89, 4564 (1967).

72. N.S. Garif, Y. Anovand, S.A. Lichkina, Bull. Acad. Soc. USSR, 450 (1970). IZV, Akad, SSSR, Serkhim, 455 (1970).

73. H. Koboyashi, I. Tsujikawa, M. Mori and Y. Yamamoto, Bull. Chem. Soc. Japan, 42, 709 (1969).

74. J. H. Enmark and R. D. Feltham, Coord. Chem. Rev., 13, 339 (1974).

75. P. T. Manoharan and P. Ganguli, Chem. Phys. Lett., 11, 281 (1971).

76. D. Wester, R.C. Edwards and D. H. Busch, Inorg. Chem., 16, 1055 (1977).

77. B.N. Figis and J.Lewis "Progress in Inorganic Chemistry" Edited by F.A. Cotton Vol. 16, 37, Inter Sciences, New Yok, (1964).

78. A.D. Walsh, J. Chem. Soc., 2266 (1953).

79. F. Hund, Z. Phys., 40, 742 (1927); 42, 93 (1927); 51, 759 (1928).

80. R.S. Mulliken, Phys. Rev., 32, 186 (1928); Rev. Mod. Phys., 4, 1 (1932).

81. D.M.P. Mingos and J.A. Ibers, Inorg. Chem., 10, 1479 (1971).

82. C.G. Pierpont and R. Elsenberg, J. Amer. Chem. Soc., 93, 4905 (1971).

83. D.M.P. Mingos, Inorg. Chem., 12, 1209 (1973).

84. P. T. Manoharan and H.B. Grey, J. Amer. Chem. Soc., 87, 3304 (1965).

85. A. Foffani, S. Pignatro, G. Distefeno and G. Innorta, J. Organometal Chem., 7, 473 (1967).

86. G. Distefeno, G. Innorta and S. Pignatro, J. Organometal Chem., 14, 165 (1968).

87. G. Innorta, G. Distefeno and S. Pignatro, Int. J. Mass Spectrum Ion. Phys., 1, 452 (1968).

88. G. Distefeno and G. Innorta, J. Organometal Chem., 14, 465 (1968).

89. J. Muller, J. Organometal Chem., 23, 38 (1970).

90. B.G.F. Johnson, J. Lewis, I.G. Williams and J.M. Wilson, J. Chem. Soc. A. 338 (1967).

91. R.B. King, Org. Mass Spectrum, 2, 657 (1969).

92. F.J. Preston and R.I. Read, Org. Mass Spectrum, 1, 71 (1968).

93. R. C. Maurya, R. K. Shukla and M. R. Maurya, J. Indian Chem. Soc., 61, 799 (1984).

94. J.H. Swinehart and P.A. Rock, Inorg. Chem., 5, 573 (1960).

95. J. Mesck and H. Wendt, Inorg. Chem. Acta., 3, 456 (1969).

96. P.A. Rock and J.H. Swinehart, Inorg. Chem., 5, 1078 (1966).

97. J. Dempire andJ. Mesck, Inorg. Chem. Acta., 2, 401 (1968).

98. J. Dempire andJ. Mesck, Inorg. Chem. Acta., 2, 443 (1968).

99. C. Andrade and D.J. Hassemer, J. Inorg. Nucl. Chem., 5, 207 (1971).

100. D.X. West and D.J. Hassemer, J. Inorg. Nucl. Chem., 32, 2717 (1970).

101. J.B. Rayner, D.I. Bustin, J.E. Earley and A.A. Vleck, Inorg. Chem., 10, 1043 (1971).

102. S.F.A. Kettle, Inorg. Chem., 4, 1661 (1965).

103. J. H. Enemark, Inorg. Chem., 10, 1952 (1971).

104. D.M.P. Mingos, W.T. Robinson and J.A. Ibers, Inorg. Chem., 10, 1043 (1971).

105. J.P. Collman, P. Farnhan and G. Dolcctti, J. Amer. Chem. Soc., 93, 1788 (1971).

106. J. H. Enemark, M.S. Quinby, L.L. Reid, M.J. Steuckaw and K.K. Walther, Inorg. Chem., 9, 2397 (1970).

107. J.R. During, W.A. McAllister, J.N. Willes Jr. and E.E. Mercer, Spectrochim Acta., 22, 109 (1966).

108. E. Mikie, Kubo, J. Mizumachi, T, Ischimori and H. Okuno, Bull. Chem. Soc. Japan, 44, 1025 (1921).

109. K. Nakamoto "Infrared and Raman spectra of Inorg. and coordination compounds" 3rd Edition, John Wiley and Son's New York (1978).

110. B.K. Sen, N. M. Ghosh and P.B. Sarkar, Indian Chem. Soc., 42, 815 (1963).

111. E. Hajmo, W. Jacob and A. Kanas, Raczniki Chem., 42, 965 (1978).

112. J. Masck and R. Privil, Inorg. Chem. Acta., 5, 499 (1971).

113. J. Masck, M.G. Bapat, B. Cosovic and J. Dempire, Coll. Czech Chem. Commn., 34, 485 (1969).

114. J. Masck and J. Dempire, Coll. Czech Chem. Commn., 34, 727 (1969).

115. J.B. Rayner, Inorg. Chem. Acta., 6, 347 (1972).

116. B. Folkesson, Acta. Chim. Scand. A., 28, 491 (1924).

117. V.I. Nefedov, Z. Wiss, Naturiss R-25 Jg., 383 (1976).

118. S. Sarkar and A. Muller, 19th International Conference Coordination Chemistry, Proceeding 2nd P-106D, Prague, Czechoslovakia (1970).

119. W. P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 872 (1959).

120. R. P. Cheny, M.G. Smic, M.Z. Hoffman, I.A. Taub and K.D. Asmeur, Inorg. Chem., 16, 2187 (1971).

121. S. Sarkar and A. Muller, Angev. Chim. (International Edition), 16, 468 (1977).

122. J.A. McCleverty "Reactions of molecule at electrodes" P-403, Ed. N.S. Hush, John Wiley and Sons Ltd. (1971).

123. J. Wei "Advances in Catalysis", 2, 57 (1975).

124. R.F.C. Johnson and J. Bhaduri, J. Chem. Soc., 96, 650 (1974).

125. B.L. Haymori and J.A. Ibers, J. Amer. Chem. Soc., 96, 650 (1974).

126. F. Bottomly, "Accounts of Chemical Research" 11, 153 (1978).

127. E.J. Baran and A. Muller, Chem. Ber., 102, 391 (1969).

128. E.J. Baran and A. Muller, Z. Anorg. Allgem. Chem., 370, 283 (1969).

129. F. Bottomly, S.G. Clarkson and S.B. Tong, J. Chem. Soc. Dalton Trans., 2344 (1974).

130. F. Bottomly and S.J. Crawford, J. Chem. Soc. Chem. Comm., 200 (1971).

131. F. Bottomly, S.G. Clarkson and E.M. Kiremire, J. Chem. Soc. Chem. Comm., 200 (1971).

132. F. Bottomly, E.M. Kiremire and S.G. Clarkson, J. Chem. Soc. Dalton Trans., 1909 (1975).

133. J.B. Godwin and T.J. Meyer, Inorg. Chem., 10, 2150 (1971).

134. S.A. Admyi, F.J. Miller and T.J. Meyer, Inorg. Chem., 11, 994 (1972).

135. F.J. Miller and T.J. Meyer, J. Amer. Chem. Soc., 93, 1294 (1971).

136. S.A. Admyi, J.N. Braddock, G.M.Brown, T.A. Ferfuson, F.J. Miller and T.J. Meyer, J. Amer. Chem. Soc., 94, 300 (1972).

137. S.A. Admyi, E.C. Johnson, F.J. Miller and T.J. Meyer, Inorg. Chem., 12, 2371 (1973).

138. P.G. Douglass and R. D. Feltham, J. Amer. Chem. Soc., 94, 5254 (1972).

139. A.J. Shortland and G. Willkinson, J. Amer. Chem. Soc. Dalton Trans., 872 (1973).

140. A. Muller, U. Seger and W. Fltzner, Inorg. Chem. Acta., 32, 165 (1979).

141. W.B. Hynes, J. Amer. Chem. Soc., 92, 532 (1970).

142. E.A. Znech, J. Chem. Soc. Chem. Comm., 1182 (1968).

143. C.R. Ungermall and K.G. Caulton, J. Amer. Chem. Soc., 98, 3862 (1976).

144. G. Dolcetti, N.W. Hoffman and J.P. Collman, Inorg. Chem. Acta., 6, 531 (1972).

145. F. Bottomly, W.V.F. Brooks, S.G. Clearson and S.B. Tong, J. Chem. Soc. Chem. Comm., 919 (1973).

146. J. H. Enemark and R. D. Feltham, Coord. Chem. Rev., 13, 339,1974.

147. C. M. Lukehart and J. N/ Troup, Inorg. Chim. Acta., 22, 81, 1974.

148. S. Sarkar, R. C. Maurya et al. Indian J. of Chem., 14A, 285, 1976.

149. R. C. Maurya and R. K. Shukla. Indian J. of Chem., 59, 340, 1982.

150. R. C. Maurya, Indian J. of Chem., 22A, 529,1983.

151. R. C. Maurya, R. K. Shukla, R. Shukla, N. Anandam, M. R. Maurya and W. U. Malik, Proc. Indian National Sc Academy., 52A, 1427, 1986.

152. S. N. Poddar and J. N. Saha, J. Indian Chem. Soc. 47, 255, 1970.

153. P. T. Manoharan and H.B. Grey, Inorg. Chem., 5, 823, 1966.

154. R. C. Maurya, R. Shukla, R. K. Shukla, N. Anandam, Proc. XXIV- ICCC, Athens, Greece, 402, 1986.

155. N. S. Gill, R. H. Nuttle, D. E. Seaife and D. W. A. Sharp, J. Inorg. Nucl. Chem., 18, 79, 1961.

156. R. C. Maurya, D. C. Gupta, R. K. Shukla, N. Anandam and M. R. Maurya, Transition Met. Chem., 12, 1427, 273-275, 1987.

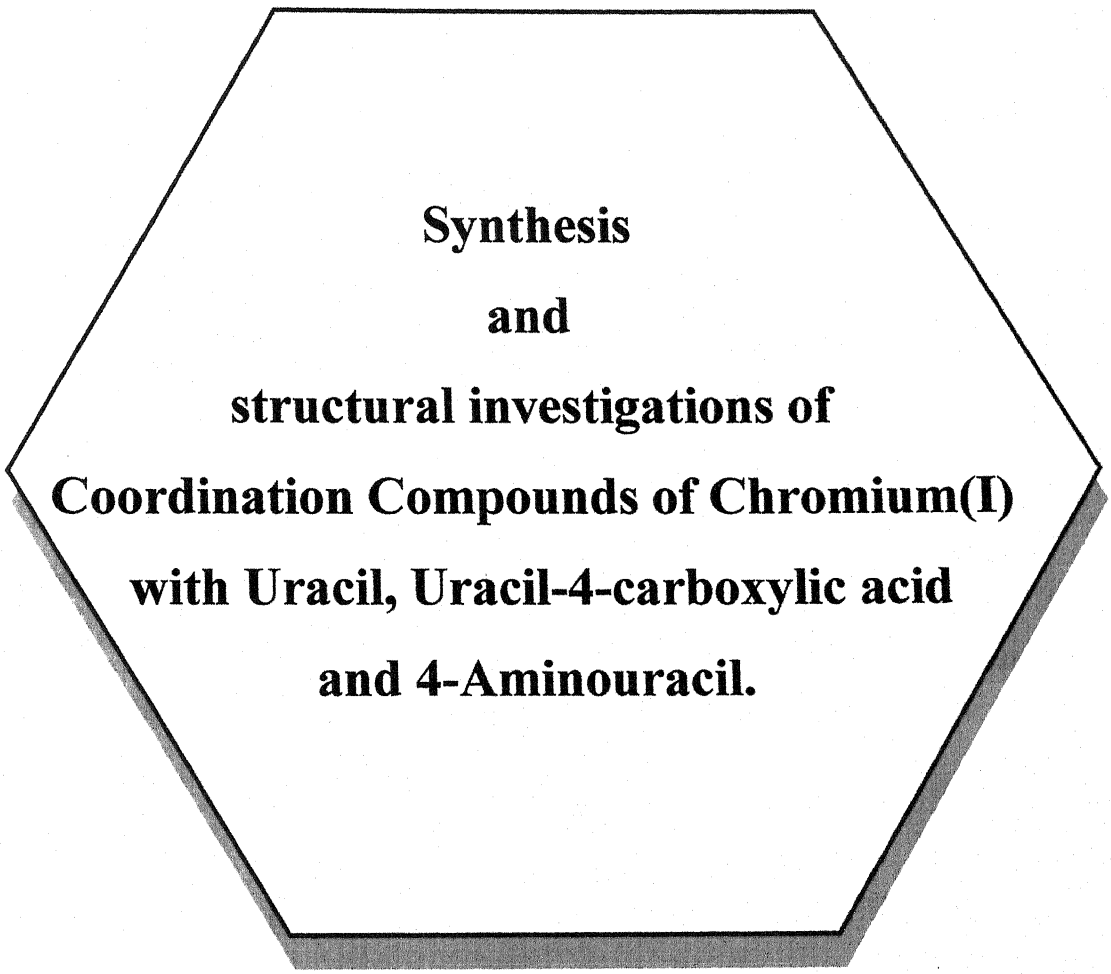
157. W. P. Griffith and G. Willkinson, J. Chem. Soc., 872, 1959.

158. R. C. Maurya, D. C. Gupta, R. K. Shukla, N. Anandam and W. U. Malik,Synth. React. Inorg. Met. Org. Chem., 16, 1243, 1986.

159. P. Griess, Chem. Ber., 12, 427, 1979.

160. R. C. Maurya, D. C. Gupta, R. K. Shukla, N. Anandam and M. R. Maurya, J. Chem. Erj. Data, 33, 215-218, 1988.

# Chapter II

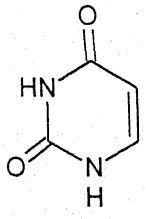

Synthesis
and
structural investigations of
Coordination Compounds of Chromium(I)
with Uracil, Uracil-4-carboxylic acid
and 4-Aminouracil.

# CHAPTER II

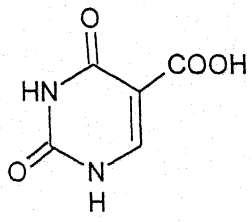
## 2.1 Introduction

Coordination compounds of uracil and their substituted of chromium (I) are synthesized and characterized in this section. Complexes of monovalent chromium are very rare **(1-14).** A survey of the literature of neutral mixed ligands nitrosyl complexes of Cr(I) reveals few reports on such compounds **(4,8,10-14)**. Although considerable importance is involve in the study of mixed ligand cyano nitrosyl $\{CrNO\}^5$ of chromium, cyano nitrosyl complexes of chromium having $\{CrNO\}^5$ electronic configuration with Uracil, Uracil-4-carboxylic acid and 4-Aminouracil have been rarely described. Further, there is no report on mixed ligand nitrosyl complexes of monovalent chromium with benzothiazoles.

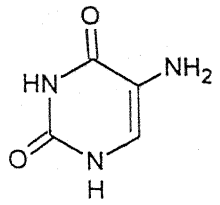
It was, therefore, thought worthwhile to synthesize and characterize some mixed ligand cyano nitrosyl $\{CrNO\}^5$ of chromium with with Uracil, Uracil-4-carboxylic acid and 4-Aminouracil.




Uracil



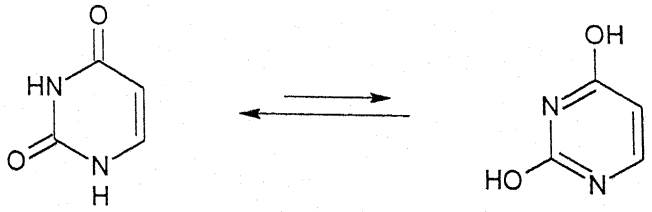

Uracil-4-carboxylic acid



4-Aminouracil

As this chapter involves the synthesis of complexes with uracil based organic compounds, it would be appropriate to discuss hare the structure, vibrational spectra, UV-VIS spectra and NMR spectra of uracil and its derivatives.

2, 4($^1$H,$^3$H)-Pyrimidinedione normally called by the trivial name Uracil has been known since 1900 when it was first isolated by hydrolysis from materials containing ribonucleic acids, such as yeast **(148)**, wheat germs **(149)**. Thymine was found much earlier from bovinethymus **(150)**. In 1901, the constitution of uracil was established by Emil Fisher **(151)**; however, 6-methyluracil was made as early as 1885 **(152)** (Scheme 1).



2,4(1H, 3H)-Pyrimidinedione

2,4-Dihydroxypyrimidine

No exhaustive and detailed review on uracils, their syntheses, structure, or their utility in heterocyclic chemistry exists. However, some aspects of uracil chemistry have been discussed with in several review series;

## I. Structure and Physical Properties

In solid state, uracil exists as the dioxo tautomer which has been shown with the aid of refined X-ray analyses from which the position of hydrogen atoms were directly determined.

Uracil crystallizes in the space group P21/a. The following list shows some parameters for the monoclinic cell.

a = 11.938 ± 0.001Å

b = 12.376 ± 0.009

c = 3.6552 ± 0.003

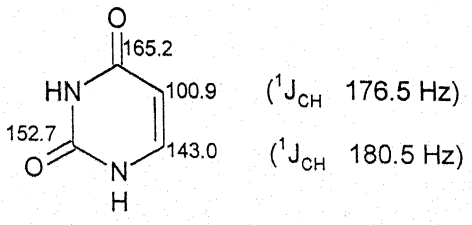
b = 120054′ + 0.4′

l (Mo Ka ) = 0.71069Å

This dioxo form is further supported by other spectroscopic data. for instance, UV-**(153)** and Raman spectroscopy **(153)** indicate that the same dioxo tautomer predominates in solution

In $^{1}$H-NMR spectroscopy (solvent:$D_2O$), 5-H and 6-H form a quadrouplet centered at δ 5.71 and 7.60, respectively, with a coupling constant of J = 8 Hz(63MI1).

As the chemical shifts of C-5 and C-6, $^{13}$C-NMR spectroscopy reveal the 5,6-double bond is highly polarized as expected for a heterocyclic enamino carbonyl compound.



The $^{15}N$-NMR data also support the dioxo structure, although all spectra are complicated by extensive, long-range $^{15}N$-H coupling and the low solubility of the material in most solvents.

The mass spectrum (MS) 70eV) of uracil shows a molecular ion at m/z 112, which expels HNCO (43 mass units) and produces a peak at m/z 69 ($C_3H_3NO^+$) and a metastable peak at m/z 42.5 **(154).** The additional fragmentation processes have been studied in detail. Protonation deprotonation sites have been discussed **(155).**

## II. Naturally Occurring Uracils; Uracils as Active Priciples

Uracils have represented, for more than 90 years ,a class of compounds that continually attract organic chemists , biochemists, medicinal chemists and photobiologists .Uracils were first detected as constituents of ribonucleic acids, from which they were prepared by hydrolysis. Nucleosides derived from uracil are called uridine, pseudouridine, and uridine phosphate, respectively. Recently, uracil moieties were detected in the antibiotic Tunicamycin **(156).**

The biosynthesis of uracil proceeds via decarboxylation of orotidin-5`-phosphate, which is formed from carbamoyl phosphate and aspartate via orotate after nucleosidation with 5-phosphoribosyl-1-diphosphate. Uracil can also be generated from cytosine by oxidative deamination using sodium hydrogensulfite.

Several uracil derivatives have been developed as drugs. Thus, methylthiouracil and propylthiouracil are thyroid inhibitors; Bucolome is an antinflammatory; and Uramustine (Uracil Mustard), Fluorouracil, and its masked compounds are anticancer agents. Aminometradine and Amisometradine are used clinically as

diuretics, and Urapidil and Ketanserin are used as antihypertensives.

Uracil nucleosides, the uridines and their derivatives, play a decisive role as biologically and pharmacologically active principles. For example, idoxuridine **(157)**, trifluridine **(157)**, and edoxuridine **(157)** show antiviral activity as an antimetabolite of thymidine; Cytarabine is used for the clinical treatment of leukemia

Naturally occurring heterocondensed uracil derivatives are methylxanthines, e.g., caffeine **(158)**, theophylline **(158),** and theobromine **(158)** show various pharmacological activities. Riboflavine (Vitamin $B_2$) acts as a coenzyme in bio-redox reactions **(159).** Uric acid is a metabolite of purine nucleoside **(160)**. Toxoflavin **(161)** and fervenuline **(161)** are antibiotics.

## III. Uracil Syntheses

The classical and primary synthetic route to uracil from formalacetic acid (made in sity from malic acid) and urea in sulfuric acid is still important **(162)**.

Some alternative syntheses use malic acid, urea, and PPA **(163)** or maleic/fumaric acid, urea, and polyphosphonic acid (PPA) **(163)**. The reaction of formylacetate with thiourea is convenient for the synthesis of 2-thiouracil. Another main synthesis involves the reaction of ureas with keto esters, diketene or acid anhydrides **(164)**. Orotic acids are synthesized from oxaloacetate and ureas in the presence of hydrogen choloride via ring transformation of hydantoin into the uracil ring system.

Treatment of the easily obtainable 2-thiouracil with chloracetic acid followed by acid hydrolysis or by oxidation with

dimethylsulfoxide (DMSO) in conc. sulphuric acid **(165)** are alternative pathways. 1,3-Dimethyluracil is transformed with urea in ethanolic sodium ethoxide into uracil.

Some more recent uracil syntheses start with propiolic acid and urea in PPA (or conc. sulfuric acid and benzene as solvent.

A broad choice of heterocondensed uracils are easily and generally accessible from heterocyclic β-enamino esters and isocyanates **(166)**. The mixed urea intermediate is smoothly cyclized with 5% aq. NaOH; the whole procedure can be carried out in a one-step reaction, when pyridine serves as solvent and base catalyst for the ring closure.

The condensation of urea with protected β-ketoesters gives 6- or 5,6-(di) substitued uracils **(167)**. By means of retro Diels-Alder splitting, norbornene condensed tricyclic dihydrouracils, accessible from aminonorbornene carboxyclic acid and 1,1`-carbonyldiimidazole, afford, upon heating, uracils **(167)** in good yield. Substituted uracils are obtained from imido esters, isocyanates, and malononitrile. Similarly N`-substituted N-cyanoacetyl ureas cyclize in an alkaline medium.

Heterocondensed uracils are easily accessible from acyllactones, -lactams, -thiollactones **(168)**, and heterocyclic β-enamino esters, especially. The latter gives a broad range of novel types of condensed systems. With the aid of the hexamethyldisilazane trimethylchlorosilane (HMDS/TMSCI) technique or the use of NaH and halosugars, respectively, simple approaches have been developed to obtain unusual nucleosides **(160)**.

## 6-AMINO-1,3-DIMETHYLURACILS

Uracil and 1,3-dimethyluracil, the title compounds of this review, are not well suited for the preparation of additional heterocyclic rings. However, 5- and 6-substituted derivatives are more promising.

Based on earlier publications by C.J. Sanderson et al. **(170)**; Ogura and Sakaguchi reported on the products formed by treatment of 6-aminouracils with dimethyl acetylenedicarboxylates (DMAD) **(169)**. Besides acylation reactions on the 5-position, a Michael adduct was found to lead to pyrido [2,3-d]pyrimidines and, after heating to to 165-175$^0$C, to pyrrolo[2,3-d]pyrimidine. These results, however, may not be correct and may be revised in the light of additional findings discussed later. Analogous reaction of dibenzoylethylene in place of DMAD gives also pyrido [2,3-d] pyrimidines or pyrrolo [2,3-d]pyrimidines or both.

Furthermore, 6-aminouracils are attacked by oxalyl chloride, diketene, and chlorocarbonylsulfenyl chloride at C-5, followed by cyclization with the amino group to give pyrrolo[2,3-d]pyrimidines, pyrido[2,3-d]pyrimidines and thiazolo[4,5-d]pyrimidines **(171)**, respectively. 6-Amino-1,3-dimethyluracil and nitrosobenzene in the presence of acetic anhydride condense to 7-phenyltheophylline via a diimine intermediate.

## 6-METHYLURACILS

6-Methyluracil derivatives possessing a functional group at C-5 have proved to be favorable to heterocyclic annullation. In particular, an electron-with drawing group, such as nitro or formyl, activates the 6-methyl group.

Thus, starting from 1,3,6-trimethyl-5-nitrouracil (10) pyrrolo[3,2-d]pyrimidines (9-deazaxanthines) can be synthesized three ways using DMF-DMA, benzaldehydes, and benzyl hallides. Condensation of the 6-methyl group with DMF-DMA and subse quent reduction of the 5-nitro group result in ring formation to give pyrrolo[3,2-d]pyrimidines. When the 6-methyluracil(1) and benzaldehydes are heated, the product depends on the solvent used. The reaction in DMF and ethanol gives 7-hydroxypyrrolopyrimidines (2) and 6-styryluracils, respectively. The latter product is cyclized to pyrrolo[3,2-d]pyrimidine (3) on reduction or treatment with triethylphosphite, and irradiations in benzene and isopropanor furnish 2 and 3, respecttively **(173)**. The stable sodium salt of 1 is isolated upon treatment with sodium ethoxide; it reacts with benzyl halides in the presence of potassium carbonate to afford 5-hydroxypyrrolo[3,2-d]pyrimidines via benzylation at the 6-methyl group.

Pyrazolo[4,3d]pyrimidine 1-oxides, though difficult to obtain, are available by a one-step synthesis from 6-bromomethyl-1,3-dimethyl-5-nitrouracil. Condensation at $0^0$C allows isolation of the alkylamino intermediates, which, in boiling ethanol, cyclize to the 1-oxides. The N-oxides, substituted with a benzyl group at N-2, undergo ring expansion in the presence of sodium ethoxide to give pyrimido[5,4-d]pyrimidines. The alkylamino intermediates are also used to synthesize pyrimido[5,4-d]pyrimidines by reduction and subsequent treatment with triethyl orthoformate.

A novel and simple approach to pyrrolo[3,4-d]pyrimidines and pyrimido[4,5-d]pyridazines is bromination of 5-formyl-1,3,6-trimethyluracil and subsequent cyclization with amines and hydrazines, respectively**(172)**. The 5-formyluracil is converted into

quinazolines by condensation with acetylacetone **(174)** or by cycloaddition of the lithium dienolate to olefins **(175)**. Aldehyde dienophiles lead to pyrano[4,3-d]pyrimidines.

5-Amino-6-methyluracil derivatives are used to synthesize various types of condensed pyrimidines. Thus, the reaction with sodium nitrite, selenium dioxide, and thionyl chlorode leads to pyrimido[4,5-d][1,2,3]triazine 3-oxides, isoselenazole[4,3-d]-pyrimidines, and isothiazole[4,3-d]pyrimidines, respec tively. 6-Arylideneamino-6-methyluracil, obtained from 5-aminouracil and benzaldehydes, condenses with diethyl oxalate and DMF-DMA to cyclize to pyrrolo[3,2-d]pyrimidines and pyrido [3,2-d]pyrimidines, respectively. Pyrimido[5,4-c]pyridazines, formed by condensation of 6-methyl-5-phenylazourac with t-butoxybis (dimethylamino) methane (BBDM), undergo reduction to a simple pyrrolo [3,2-d]pyrimidine(9-deazaxanthine).

## 2.2 Experimental

### (a) Materials Employed

Hydroxylaminehydrochloride (BDH, England), Potassium Cyanide (May and Baker), Chromic acid were used as such. Uracil, Uracil-4-carboxylic acid and 4-Aminouracil were used as supplied.

Distilled water was used in all the operations.

### (b) Analysis of the constituent elements:

(i) Carbon, Hydrogen, Nitrogen and sulphur present in the synthesized complex were estimated micro analytically.

### (ii) Estimation of chromium:

For the estimation of the chromium as chromic oxide ($Cr_2O_3$), the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. chromium was precipitated as chromic hydroxide by means of dil. ammonium hydroxide. chromic hydroxide, when ignited, was converted into $Cr_2O_3$. Repeated heating, cooling and weighing were carried out until constant weight obtained.

### (c) Physical Methods

### (i) Conductance Measurements

Conductances were measured in analytical grade dimethyl sulpoxide (DMSO) and dimethyl formamide (DMF) using dip type cell on Toshniwal Conductivity Bridge at the department of chemistry, Atarra P.G. College, Atarra.

**(ii) Magnetic susceptibility measurements**

Magnetic susceptibility measurements were made at room temperature by the Gouy method. A magnetic field strength of 8500 gauss was employed. The apparatus was calibrated using Cobalt mercury thiocyanate, $Hg[Co(NCS)_4]$. The diamagnetic corrections were computed using Pascal's constant **(16-17)**. For calculation of effective magnetic moment, following equation has been used and data obtained are summarized in table 2.7

Effective magnetic moment ($\mu$eff) = $2.84\left(x_m^{corr}.T\right)^{1/2}$

Where T= temperature in absolute scale, and

$x_m^{corr.}$ = corrected molar susceptibility

**(iii) Infrared measurements**

Infrared spectra (4000-450 $cm^{-1}$) of the uncoordinated ligands and synthesized complexes were recorded in nujol mulls supported between KBr pellets on Perkin Elmer (RXI) spectrometer (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

**(iv) UV-VIS spectral measurements**

UV-VIS spectra of the uncoordinated ligands and synthesized complexes were recorded on Perkin Elmer lambda 15 UV-VIS spectrophotometer ranging from (260-700 nm) (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

(v) **NMR measurements**

NMR spectra of the uncoordinated ligands and synthesized complexes were recorded on Brucker DRX-300MHz FT NMR using DMSO as solvent.

(vi) **Molecular weight determination**

Molecular weight determination of the synthesized complexes were made by Rast's method.

## 2.3 Preparation of the parent compound

Potassium pentacynonitrocylchromate(I) monohydrate was prepared by the method reported by Wilkinson et. al. as follows:

Chromium trioxide ($CrO_3$) (7 gm) was added to a cold saturated solution of KOH (20 gm) with ice cooling. Saturated aqueous KCN (35 gm) was then added and the mixture filtered. $NH_2OH.HCl$ (8 gm) was added to the filtrate and the solution was heated on steam both for two hours, and then filtered and cooled, and the filtrate poured with stirring into ethanol (95%, 25 ml.). The precipitate was dissolved in minimum quantity of water and the compound again precipitated with ethanol; on crystallization from water gave bright crystals. Compound was characterized by elemental analysis and IR spectroscopy.

The observed results are as follows:

| | *K (in %)* | *Cr (in %)* | *C (in %)* | *N (in %)* | *$H_2O$ (in %)* |
|---|---|---|---|---|---|
| Experimental | 33.8 | 15.8 | 18.05 | 24.5 | 5.1 |
| Calculated | 33.8 | 15.1 | 18.03 | 24.2 | 5.2 |

| I.R.; | $\nu(NO)^+$ | $\nu(CN)$ | |
|---|---|---|---|
| Found | (reported) | Found | |
| (reported) | | | |
| 1645 vs | (1645 vs) | 2135 | (2135 s) |
| | | 2192 | (2195 s) |

## 2.4 PREPARATION OF COMPLEXES

### (a) Preparation of $[Cr(NO)(CN)_2(Url)_2(H_2O)]$

A filtered acidified (with acetic acid) aqueous solution (50 ml) of potassium salt of the pentacynonitrocylchromate(I) monohydrate (0.1M) was added into an aqueous alcoholic solution (1:1 10 ml) of the uracil ligand (0.02M). The resulting greenish-brown solution was heated over hot plate for 25 minutes at fixed 80°C temperature. Carbon dioxide was allowed to bubble through the solution for few hours, to chase the liberated HCN, when a coloured solid was precipitated. The precipitate was filtered, washed several times with distilled water and finally with ethanol and dried in vacuum desiccator over silica gel at room temperature to a constant weight.

### (b) Preparation of $[Cr(NO)(CN)_2(Url\text{-}4\text{-}CA)_2(H_2O)]$

A filtered aqueous solution (50 ml) of potassium salt of the pentacynonitrocylchromate(I) monohydrate (0.1M) was added into an aqueous alcoholic solution (1:1 10 ml) of the uracil-4-carboxylic acid ligand (0.02M). The resulting

light brownish solution was heated over hot plate for 25 minutes at fixed 80°C temperature. Carbon dioxide was allowed to bubble through the solution for few hours, to chase the liberated HCN, when a coloured solid was precipitated. The precipitate was filtered, washed several times with distilled water and finally with ethanol and dried in vacuum desiccators over silica gel at room temperature to a constant weight.

### (c) Preparation of$[Cr(NO)(CN)_2(4\text{-Amino Url})_2(H_2O)]$

A filtered aqueous solution (50 ml) of potassium salt of the pentacynonitrocylchromate(I) monohydrate (0.1M) was added into an aqueous alcoholic solution (1:1 10 ml) of the 4-Aminouracil ligand (0.02M). The resulting yellowish brown solution was heated over hot plate for 25 minutes at fixed 80°C temperature. Carbon dioxide was allowed to bubble through the solution for few hours, to chase the liberated HCN, when a coloured solid was precipitated. The precipitate was filtered, washed several times with distilled water and finally with ethanol and dried in vacuum desiccator over silica gel at room temperature to a constant weight. The obtained analytical data are given in table 2.2.

## 2.5 PROPERTIES OF COMPLEXES

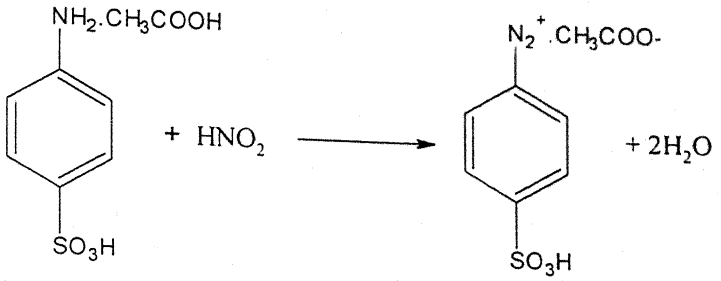
All the complexes are coloured solid (Table 2.3). They are stable in air. Solubilities of these complexes in different solvents are given in (Table 2.3). The complexes are thermally stable and do not melt or decompose up to 300°C (Table 2.3).

They decompose in dil. acids and alkalis only on heating. Both complexes after decomposition with KOH followed by acidifying with acetic acid give a pink coloured with few drops of Griess reagent**(29)**. The appearance of pink colour is most probably is due to the NO group of the complex which after decomposition changes to $NO_2^-$ ion and form a pink dye with the reagent. This indicates the presence of NO group in the synthesized complexes. The probable reaction scheme for the Griess reagent is summarized as below.

### PROBABLE REACTION SCHEME FOR THE GRIESS REAGENT

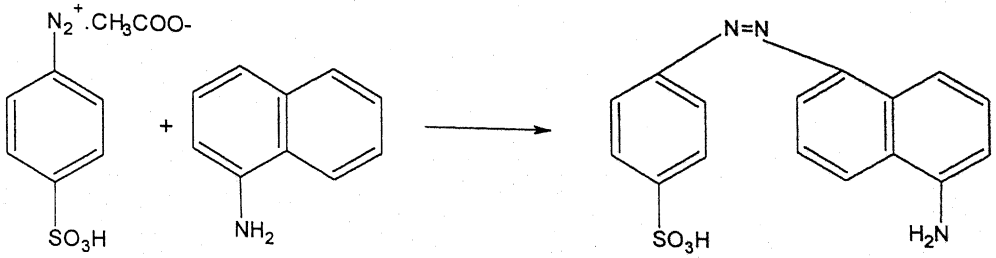
$$[Cr(NO)(CN)_2(L)_2(H_2O)] \xrightarrow[\text{Decomposition}]{KOH,\ H_2O} NO_2^- + \text{Chromium oxide}$$

$$NO_2^- + H^+ \longrightarrow HNO_2$$




Sulphanilic Acid

(A component of Griesss Reagent)




Naphthylamine

(Another component of Griess reagent)

Pink coloured dye + $CH_3COOH$

## 2.6 RESULTS AND DISCUSSION

The mixed ligand complexes $[Cr(NO)(CN)_2(L)_2(H_2O)]$ were prepared according to the equation

$$K_3[Cr(NO)(CN)_5].H_2O + 2L \xrightarrow[H_2O]{CH_3COOH} [Cr(NO)(CN)_2(L)_2H_2O] + H_2O + 3CH_3COOK + 3HCN$$

Where L = Uracil, Uracil-4-carboxylic acid or 4-Aminouracil

The partial replacement of the cyano groups in the hexa-co-ordinated parent complex $K_3[Cr(NO)(CN)_5].H_2O$ by two molecules of ligand arises from the *trans* effect of the NO group. Studies by Raynor and coworkers **(35)** on stepwise aquation of the pentacyanonitrocylchromate(I),anion $[Cr(NO)(CN)_5]^{3-}$ and thereby

attaining the tris(aqua)species of composition $[Cr(NO)(CN)_2.(H_2O)_3]$ favour the above reaction scheme.

Compounds were characterized on the basis of the following results.

**(a) Conductance Measurements**

The molar conductance values measured in $10^{-3}$ M dimethylsulphoxide as well as in dimethylformamide solutions. The conductance data are in agreement with the non-electrolytic nature **(8)** of these complexes.

**(b) Magnetic Measurements**

The magnetic moment values of the synthesized complexes at room temperature are presented in Table 2.7. An observation of the table shows that the magnetic moment values of the complexes are closed to the spin only values for one unpaired electron (1.73 B.M.)

**(c) Infrared spectral studies**

The IR spectra of some of the reported complexes containing coordinated Uracil, Uracil-4-carboxylic acid, 4-Aminouracil and coordinated NO, CN of the synthesized complexes are presented in table 2.10 respectively.

A comparison of the infrared spectra of the parent compound $K_3[Cr(NO)(CN)_5].H_2O$ and of the synthesized complexes suggests that the appearance of the very strong band in the region 1700-1705 $cm^{-1}$ in these complexes, is of coordinated $NO^+$ stretching. The negative shift of approximately 60 $cm^{-1}$ in these complexes compared to the parent compound is perhaps due to the non-electrolytic nature of these complexes.

Both the synthesized compounds reported here show a strong band in the region 2140-2160 $cm^{-1}$. This band is assigned

for ν (CN), which is in accordance with assignment made for other reported complexes.

The ligand Uracil possesses 3 possible donor sites; two cyclic nitrogen and one ketonic group in the ring respectvely. Further the cyclic nitrogen involved in coordination through the N atom. Coordination through N in the cyclic nitrogen group amino group invariably results in the increase in at least 40 $cm^{-1}$. In the complex of uracil 4–carbo xylic acid studied here, the IR frequency of cyclic nitrogen ring is essentially changed, thereby, suggesting the cyclic nitrogen of this ligand has been participate in the coordination.

In the IR spectra of complex with 4–amino uracil the bands at 644 $cm^{-1}$ and suffered a lower shift of 611 $cm^{-1}$ indicating that the metal nitrogen coordination. Hambright et al **(* 465)** confirmed metal nitrogen coordination in the large series of complexes of Zn(II), Cu(II), Ni(II), Coordination(II) and Pt(II).

The nitrile group may be involved in coordination through either the nitrogen or the triple bond. Coordination through nitrogen of the nitrile group invariably results in an increase in ν(CN) **(32)** by at least 30$cm^{-1}$.

The appearance of other broad bands in the range 3550-3580 $cm^{-1}$ and 3375-3400 $cm^{-1}$ in all the complexes is due to ν(OH) coordinated water **(7)**.

The analytical data and all the evidences presented above suggest the formulation of these complexes as. Since all these complexes show one CN stretching band and one NO stretching band it is reasonable to propose an octahedral structure **(10)** where

CN is trans to CN and L ligands are trans to each other in equatorial position , whereas NO is trans to water in axial position.

## 2.7 SUMMARY

The novel mixed ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium general formula $[Cr(NO)(CN)_2(L)_2H_2O]$( where L= uracil, uracil-4-carboxylic acid and 4-Amino uracil have been prepared by the interaction of potassium pentacyanonitrosyl chromate (I) monohydrate with the said ligands. The complexes, which have been characterized by elemental analysis, magnetic measurements, conductance studies, molecular weight determinations, infrared spectral studies, UV-VIS spectral analysis and NMR studies, contain chromium(I) in a low spin $\{CrNO\}^5$ electron configuration.

A suitable octahedral structure where CN is *trans* to CN and L is *trans* to L, and NO is *trans* to water is proposed for all the complexes. It is observed that –

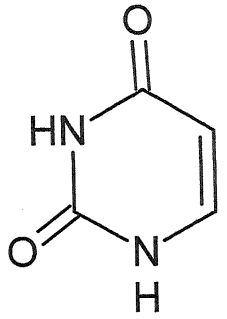
**(i)** All the complexes are air stable coloured solids.

**(ii)** They are soluble in DMF, DMSO, ethanol and methanol but insoluble in nitrobenzene and ethyl acetate.

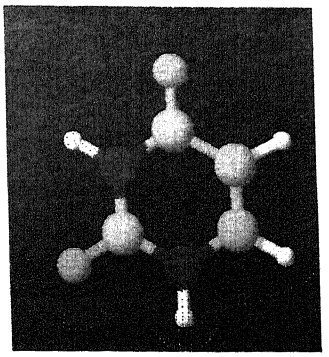
**(i)** All the complexes contain $\{CrNO\}^5$ electron configuration.

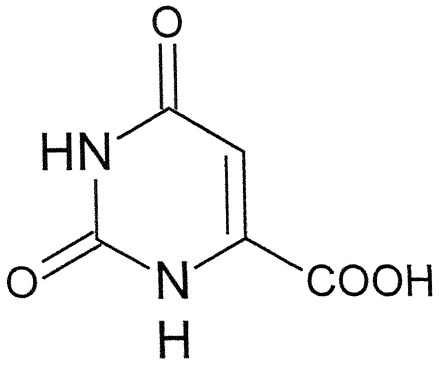
**(iv)** All the compounds are thermally stable upto 300°C.

*(v)* All of them give pink colour with Griess Reagent.

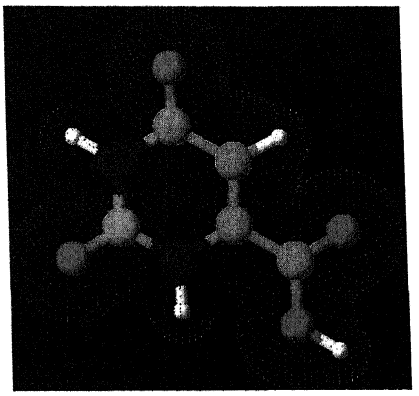


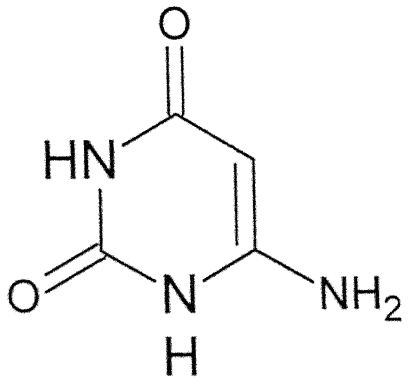

Uracil



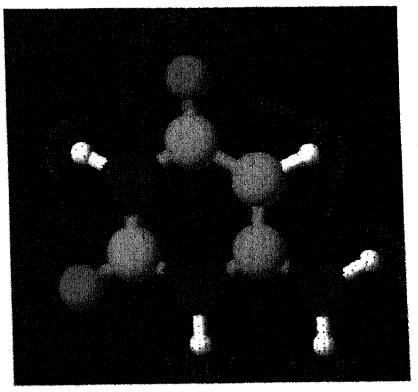



Uracil-4-carboxylic acid






4-Aminouracil



## *Table 2.1*

## *I.U.P.A.C. Name and Electron Configuration of the synthesized complexes*

| *S. No.* | *Compound* | *I.U.P.A.C. Name* | *Electron Configuration* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | Aquadicyanodi(Uracil)-nitrosylchromium (I) | $\{CrNO\}^5$ |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | Aquadicyanodi(Uracil 4–carboxylic acid)-nitrosylchromium (I) | $\{CrNO\}^5$ |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | Aquadicyanodi(4 – Amino uracil)-nitrosylchromium (I) | $\{CrNO\}^5$ |

## *Table 2.2*

### *Analytical Data of the Complexes*

| *S. No.* | *Compound* | *% Cr Found (Calc.)* | *% C Found (Calc.)* | *% H Found (Calc.)* | *% N Found (Calc.)* |
|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 13.50 (13.74) | 25.30 (25.40) | 2.11 (2.13) | 33.00 (33.33) |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 10.90 (11.15) | 25.65 (25.76) | 1.70 (1.73) | 26.79 (27.04) |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 12.56 (12.75) | 23.40 (23.53) | 2.41 (2.46) | 37.54 (37.74) |

## *Table 2.2 A*

### *Molecular weight of the Complexes*

| S.No. | Compound | Molecular weight | |
|---|---|---|---|
| | | Found | Calculated |
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 376.02 | 378.20 |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 464.03 | 466.22 |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 405.34 | 408.23 |

## Table 2.3

## Colour, Decomposition Temperature and % Yield of the Complexes

| S. No. | Compound | Colour | Decomposition Temperature (°°C) | % Yield |
|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | Greenish Brown | 310 | 56 |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | Light Brown | 310 | 54 |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | Yellowish Brown | 312 | 52 |

## *Table 2.4*

### *Solubilities of the Complexes in different Solvents*

| *S. No.* | *Compound* | *DMF* | *DMSO* | *EtOH* | *MeOH* | *Nitrobenzene* | *Ethylacetate* |
|---|---|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 50% | 55% | 25% | 20% | Insoluble | Insoluble |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 45% | 50% | 20% | 15% | Insoluble | Insoluble |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 50% | 45% | 30% | 20% | Insoluble | Insoluble |

## *Table 2.6*

### *Dehydration temperature and molecular weight of the Complexes*

| *S. No.* | *Compound* | *Dehydration temperature(°C)* | *molecular weight)* | |
|---|---|---|---|---|
| | | | *Found* | *Calculated* |
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 112 | 376.02 | 378.20 |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 115 | 464.03 | 466.22 |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 115 | 405.34 | 408.23 |

## *Table 2.7*

### *Magnetic and ESR data of the Complexes*

| *S. No.* | *Compound* | $\mu_{eff}$ *(B.M.)* | *'g'* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 1.72 | 1.984 |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 1.70 | 1.985 |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 1.72 | 1.983 |

## *Table 2.8*

### *Important IR spectral bands and their assignments (Reported Compounds)*

| *S. No.* | *Compound* | $\nu_{(N-H)}$ | | $\delta_{(N-H)}$ | | *Ref.* |
|---|---|---|---|---|---|---|
| | | *Asymmetric* | *Symmetric* | | | |
| 1 | $[Hg(anln)_2Cl_2]$ | 3346 (m) | 3250 (m) | 1600 (w), | 1575 (m) | ***21*** |
| 2 | $[Hg(anln)_2Br_2]$ | 3346 (m) | 3286 (m) | 1600 (m), | 1572 (m) | ***21*** |
| 3 | $[Hg(o\text{-}told)_2Cl_2]$ | 3292 (m) | 3262 (m) | 1590 (sh), | 1575 (m) | ***21*** |
| 4 | $[Hg(o\text{-}told)_2Br_2]$ | 3316 (m) | 3230 (m) | 1585 (m), | 1572 (m) | ***21*** |
| 5 | $[Hg(m\text{-}chloroanln)_2Cl_2]$ | 3280 (m) | 3184 (m) | 1590 (m), | 1575 (sh) | ***21*** |
| 6 | $[Zn(m\text{-}chloroanln)_2Cl_2]$ | 3290 (m) | 3250 (m) | 1586 (s), | - | ***22*** |
| 7 | $[Zn(p\text{-}chloroanln)_2Cl_2]$ | 3286 (m) | 3240 (m) | 1596 (s), | 1548 (s) | ***22*** |
| 8 | $[Zn(p\text{-}chloroanln)_2Br_2]$ | 3280 (m) | 3240 (m) | 1596 (s), | 1580 (s) | ***22*** |

## *Table 2.9*

### *Important IR spectral bands and their assignments (Reported Compounds)*

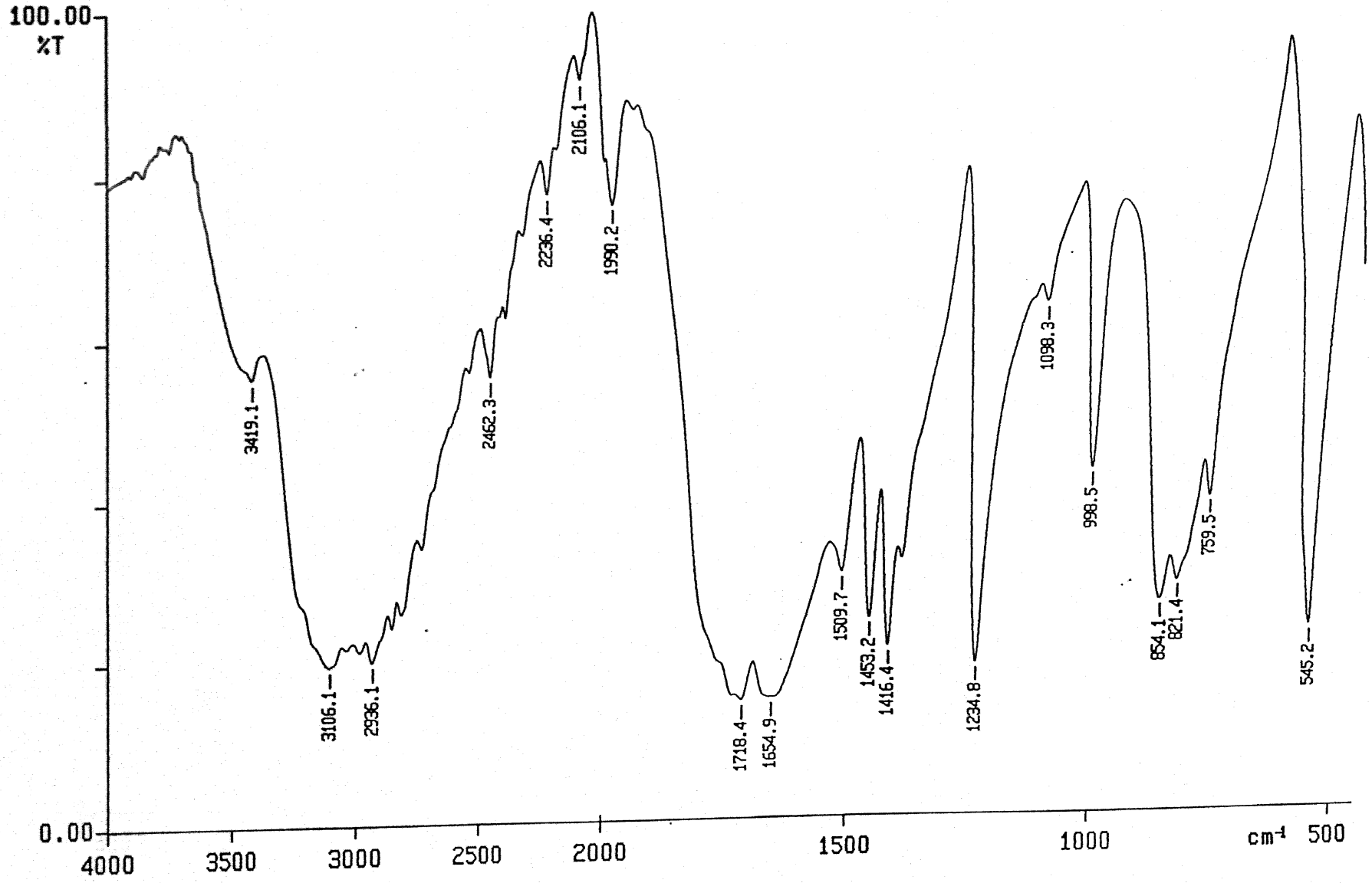
| S. No | Compounds | NO ($cm^{-1}$) | (CN) ($cm^{-1}$) | (Cr-N) ($cm^{-1}$) | (Cr-NO) ($cm^{-1}$) |
|---|---|---|---|---|---|
| 1 | $K_3[Cr(CN)_5NO].2H_2O$ | 1605 (vs) | 2137 (s)<br>2195 (sh) | 620 (w) | 610 (m) |
| 2 | $[Cr(NO)(Cl)(diars)].ClO_4$ | 1690 (vs) | 2195 (sh) | - | - |
| 3 | $[Cr(NO)(NH_3)_5].Cl_2$ | 1670 (vs) | - | - | - |
| 4 | $[Cr(NO)(H_2O)_5].Cl_2$ | 1747 (vs) | - | - | - |
| 5 | $[Cr(NO)(MeOH)_5].Cl_2$ | 1919 (vs) | - | - | - |
| 6 | $[Cr(NO)(EtOH)_5].Cl_2$ | 1708 (vs) | - | - | - |
| 7 | $[Cr(NO)(ONO)_5].Cl_2$ | 1708 (vs) | - | - | - |
| 8 | $([Cr(NO)(CN)_2(dipy)].Cl_2$ | 1694 (vs) | 2157(s)<br>2133(sh) | 612 | 600 |
| 9 | $[Cr(NO)(acac)_5].Cl_2$ | 1692 (vs) | - | 610 | 592 |
| 10 | $[Cr(NO)(DTC)_2(H_2O)].Cl_2$ | 1705 (vs) | - | 620 | 575 |

## *Table 2.10*

### *Important IR spectral bands and their assignments*

| S. No. | Compound | $\nu_{(NO)}^{+}$ | $\nu_{(CN)}$ | $\nu_{(NH)}$ | $\nu_{(OH)}$ |
|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Url)_2(H_2O)]$ | 1705(vs) | 2140(s) | 3250(br)<br>3160(br) | 3550(br)<br>3380(br) |
| 2. | $[Cr(NO)(CN)_2(Url\ 4\text{–}CA)_2(H_2O)]$ | 1700(vs) | 2150(s) | - | 3575(br)<br>3400(br) |
| 3. | $[Cr(NO)(CN)_2(4\text{–}A\ Url)_2(H_2O)]$ | 1710(vs) | 2145(s) | | 3570(br)<br>3410(br) |

PERKIN ELMER

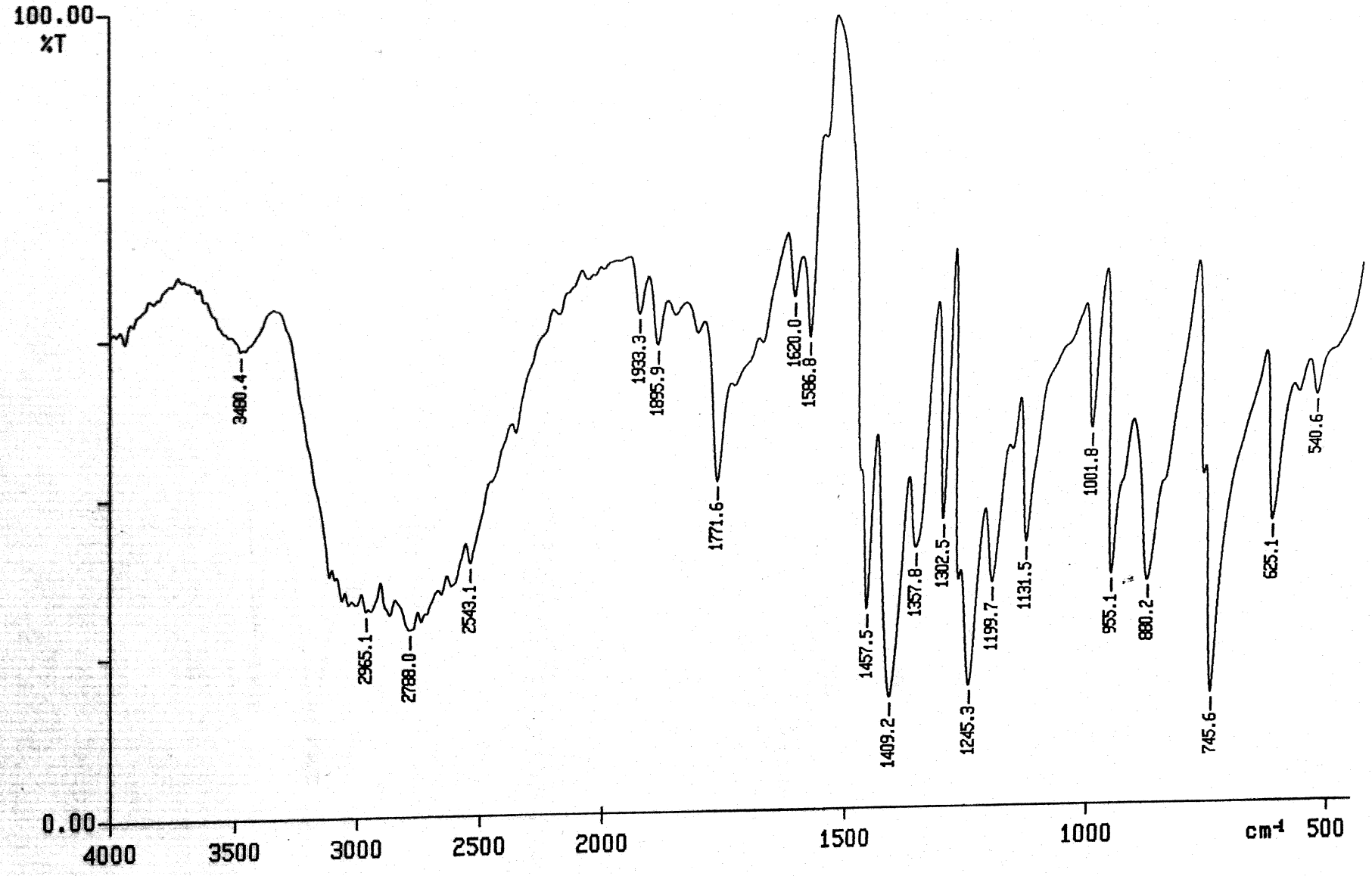



04/01/08 10:43 AH, CODE- A
X: 4 scans, 4.0cm-1, flat, smooth, abex

SAIF NO - 6809

**COORDINATION COMPOUND WITH URACIL**

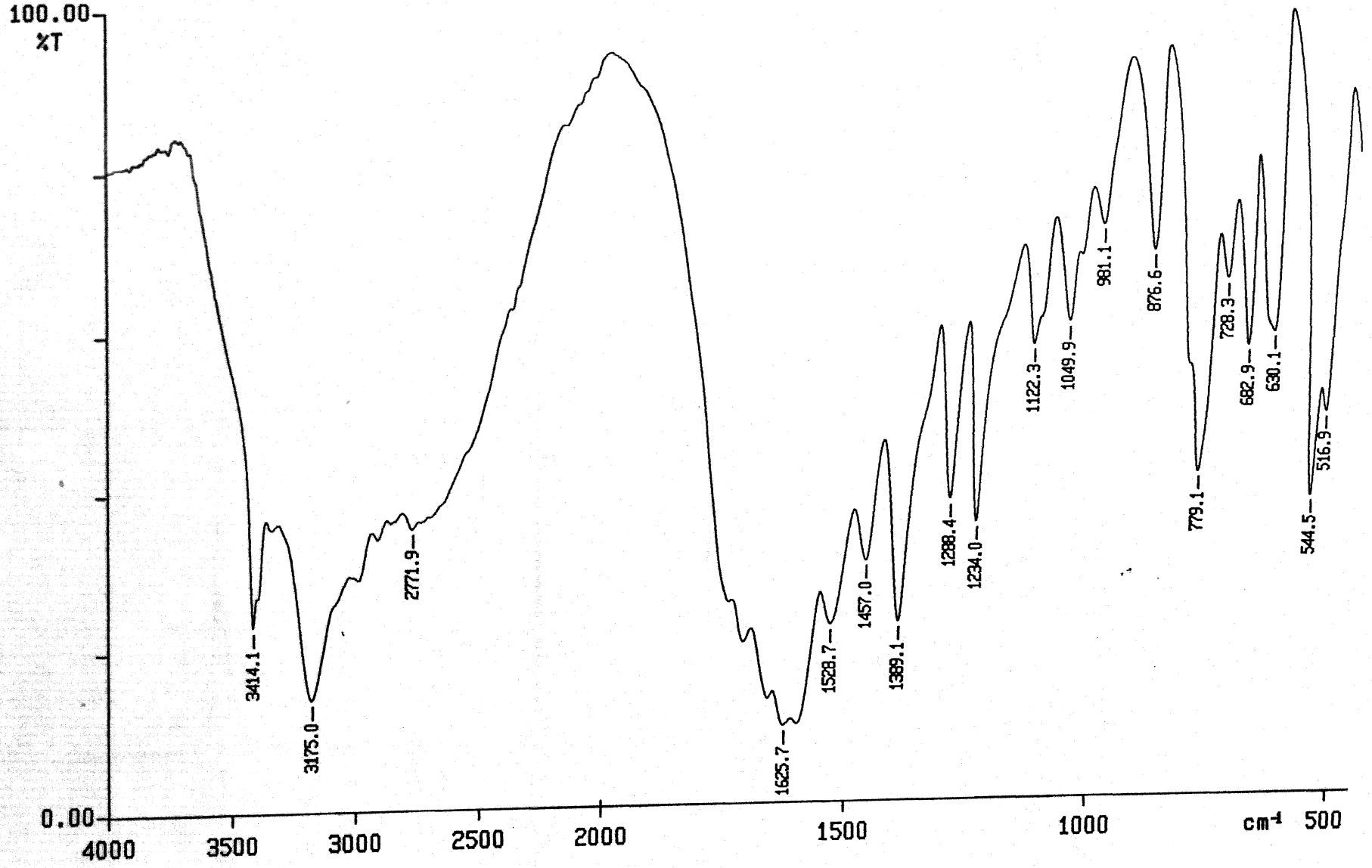
PERKIN ELMER




04/01/08 11:04 AH, CODE- J
X: 4 scans, 4.0cm-1, flat, smooth, abex
SAIF NO - 6809

**COORDINATION COMPOUND WITH URACIL-4-CORBOXYLIC ACID**

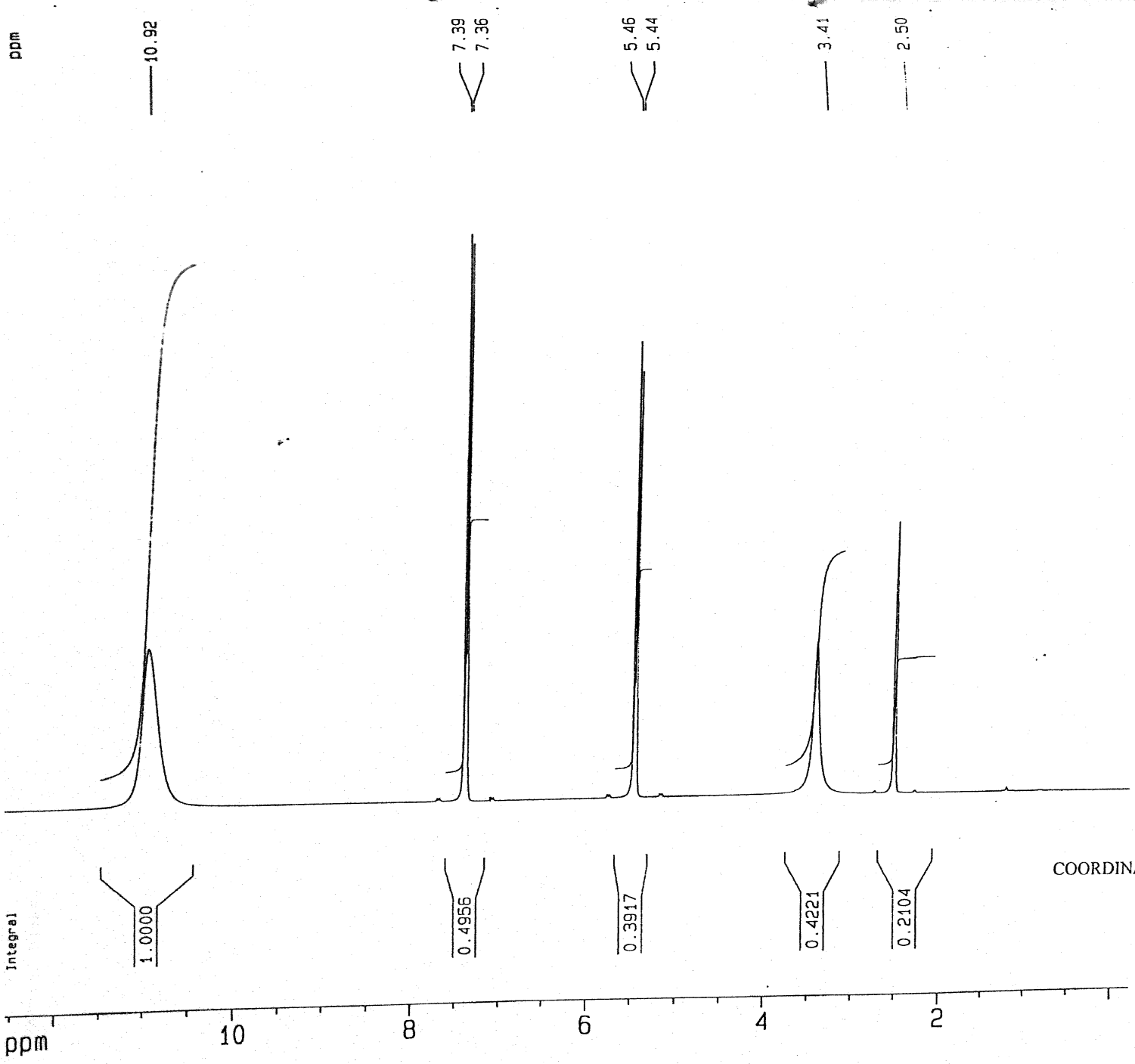
PERKIN ELMER




04/01/08 10:48 AH, CODE- C
X: 4 scans, 4.0cm-1, flat, smooth, abex

SAIF NO - 6809

**COORDINATION COMPOUND WITH 4-AMINO URACIL**




Current Data Parameters

| | |
|---|---|
| NAME | 6809 a |
| EXPNO | 1 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20040303 |
| Time | 12.34 |
| INSTRUM | DRX300 |
| PROBHD | 5 mm Multinu |
| PULPROG | zg |
| TD | 32768 |
| SOLVENT | DMSO |
| NS | 24 |
| DS | 0 |
| SWH | 8680.556 Hz |
| FIDRES | 0.264910 Hz |
| AQ | 1.8874868 sec |
| RG | 128 |
| DW | 57.600 usec |
| DE | 6.00 usec |
| TE | 298.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 6.88 usec |
| PL1 | -3.00 dB |
| SF01 | 300.1321300 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 16384 |
| SF | 300.1300010 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.10 Hz |
| GB | 0 |
| PC | 1.20 |

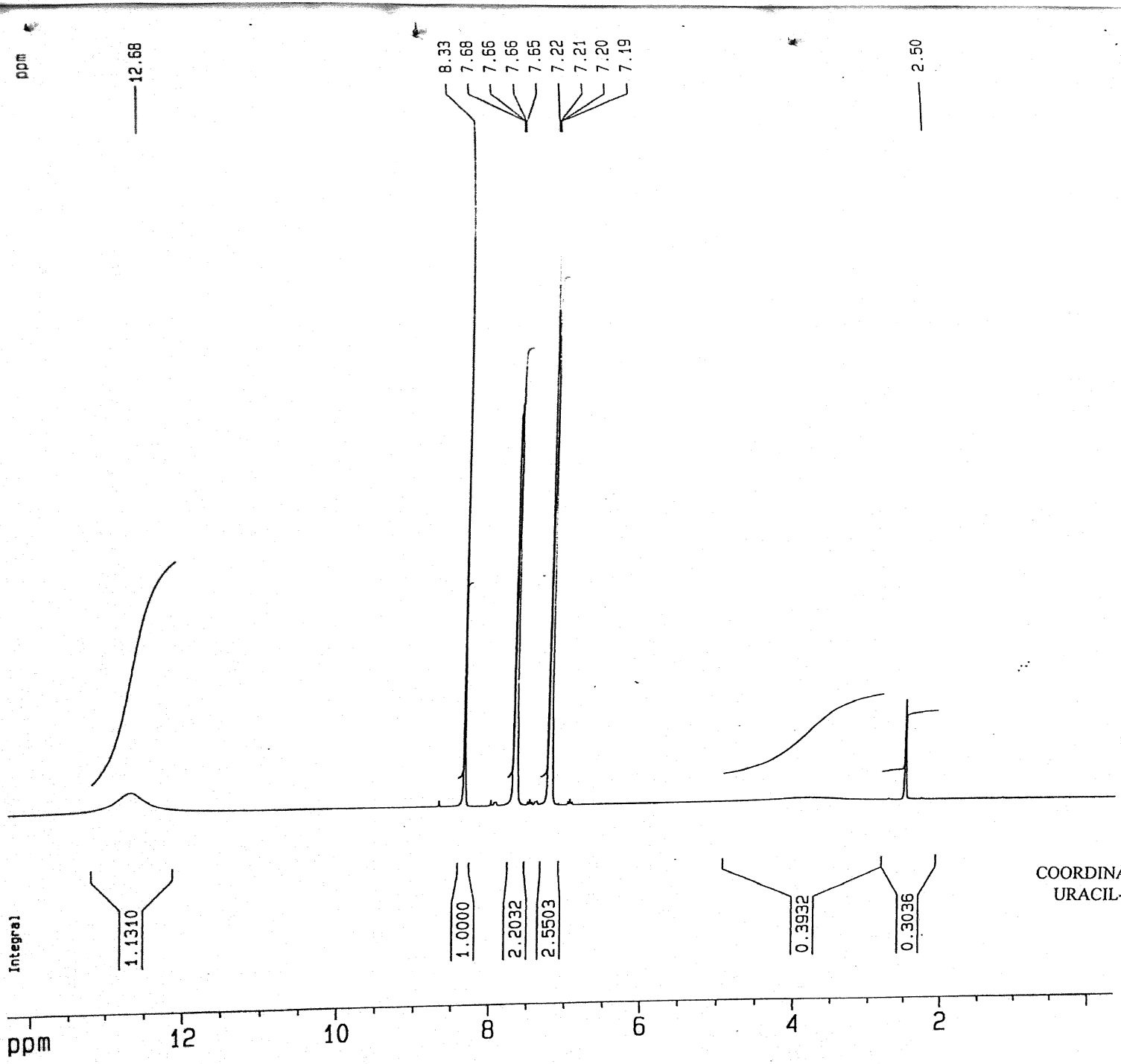
1D NMR plot parameters

| | |
|---|---|
| CX | 20.00 cm |
| F1P | 12.549 ppm |
| F1 | 3766.24 Hz |
| F2P | -0.226 ppm |
| F2 | -67.97 Hz |
| PPMCM | 0.63876 ppm/cm |
| HZCM | 191.71046 Hz/cm |

COORDINATION COMPOUND WITH URACIL

A

RSIC NO.6809




Current Data Parameters
NAME 6809
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040303
Time 15.40
INSTRUM DRX300
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT DMSO
NS 32
DS 0
SWH 8680.556 Hz
FIDRES 0.264910 Hz
AQ 1.8874368 sec
RG 32
DW 57.600 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec

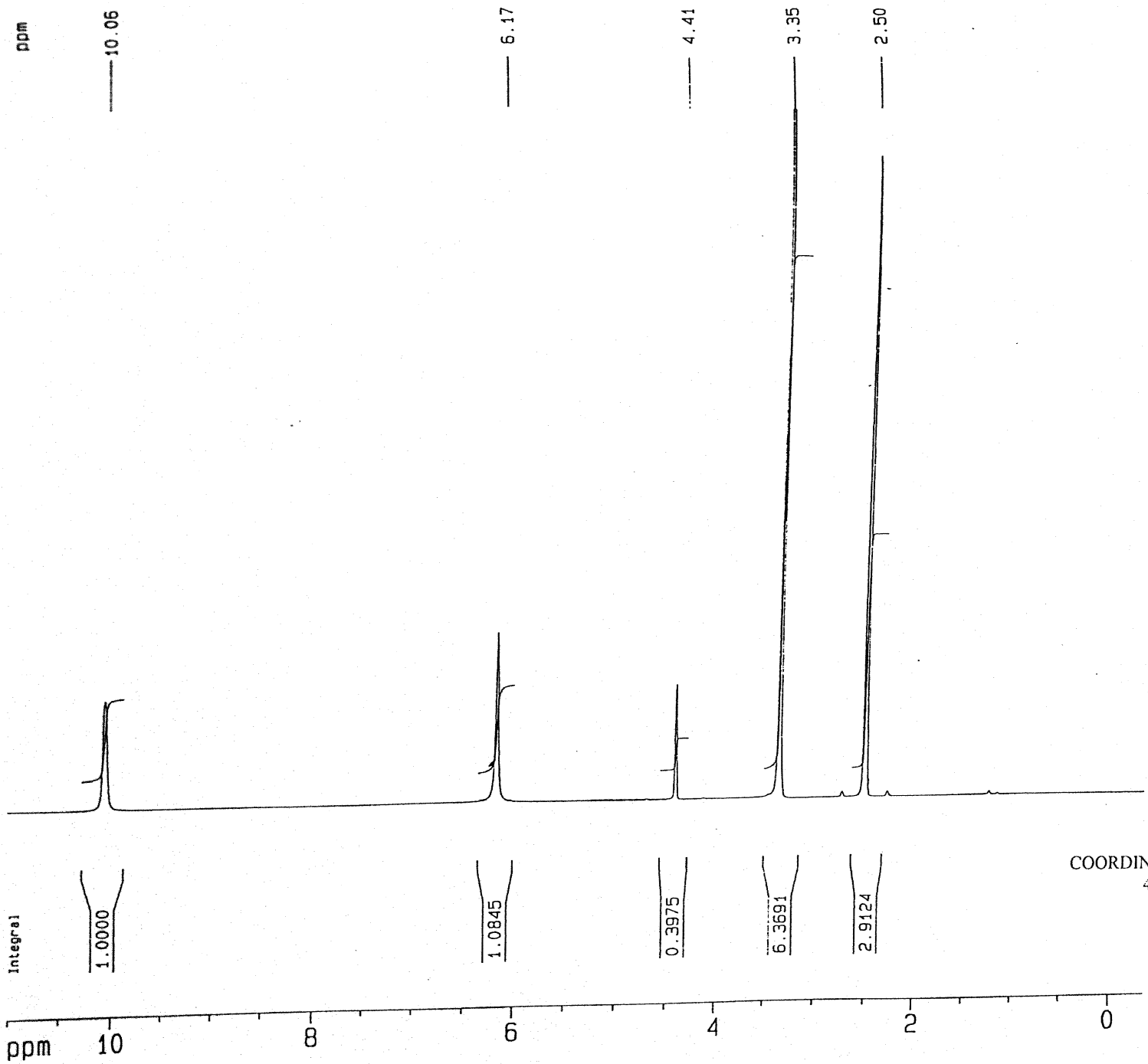
========== CHANNEL f1 ==========
NUC1 1H
P1 6.88 usec
PL1 -3.00 dB
SF01 300.1321300 MHz

F2 - Processing parameters
SI 16384
SF 300.1300010 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.20

1D NMR plot parameters
CX 20.00 cm
F1P 14.294 ppm
F1 4290.17 Hz
F2P -0.345 ppm
F2 -103.69 Hz
PPMCM 0.73199 ppm/cm
HZCM 219.69305 Hz/cm

COORDINATION COMPOUND WITH
URACIL-4-CARBOXYLIC ACID

J




```
Current Data Parameters
NAME                  6809 c
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20040303
Time                 12.28
INSTRUM              DRX300
PROBHD       5 mm Multi:u
PULPROG                zg
TD                  32768
SOLVENT              DMSO
NS                     24
DS                      0
SWH             8680.555 Hz
FIDRES          0.264910 Hz
AQ              1.8874808 sec
RG                     25?
DW                57.600 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                 6.89 usec
PL1               -3.00 dB
SFO1        300.1321300 MHz

F2 - Processing parameters
SI                    16384
SF          300.1300010 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.20

1D NMR plot parameters
CX                  20.00 cm
F1P                11.001 ppm
F1                3301.65 Hz
F2P                -0.345 ppm
F2                -103.69 Hz
PPMCM           0.56734 ppm/cm
HZCM          170.27701 Hz/cm
```

COORDINATION COMPOUND WITH
4-AMINO URACIL

C
RSIC NO.6809

# Chapter III

## Synthesis and physicochemical studies of new cyanonitrosyl $\{CrNO\}^5$ coordination compounds of Chromium with 5–Fluoro uracil and 5–methyl uracil.

# Chapter III :

# Synthesis and physicochemical studies of new cyanonitrosyl $\{CrNO\}^5$ coordination compounds of Chromium with 5–Fluoro uracil and 5–methyl uracil.

## 3.1 Introduction

In chapter II, synthesis and physiochemical studies of some mixed ligand cyanonitrosyl $\{CrNO\}^5$ complexes of chromium with some substitutes 5–Fluoro uracil and 5–methyl uracil have been discussed. As a part of our programme to synthesize and characterize some neutral mixed ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended using some more benzothiazoles derivatives

In recent years, a great deal of interest has been shown to the study of neutral mixed-ligand cyanonitrosyl complexes of chromium having $\{CrNo\}^5$ electron configuration.* No attempts have been made so for to isolate cyanonitrosyl complexes of monovalent chromium with some substituted uracil. We therefore, report here the first synthesis of neutral mixed ligand cyanonitrosyl

complexes of chromium with 5–Fluoro uracil and 5–methyl uracil. The present chapter describes the results of such studies.

## 3.2 EXPERIMNTAL

### (a) Materials used:

5–Fluoro uracil and 5–methyl uracil were used as such as supplied by Aldrich Chemical Company, USA. Hydroxylaminehydrochloride and Chromic acid were supplied by SD Fine Mumbai. Potassium Cyanide was procured from May and Baker Limited, Dagenham. Distilled water was used in all the operations.

### (b) Analysis of the constituent elements:

(i) Carbon, hydrogen and nitrogen were estimated micro-analytically.

(ii) **Estimation of chromium**

For the estimation of the chromium as chromic oxide ($Cr_2O_3$), the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by means of dil. ammonium hydroxide. chromic hydroxide, when ignited, was converted into $Cr_2O_3$. Repeated heating, cooling and weighing were carried out until constant weight obtained.

## (c) Physical Methods:

### (i) Conductance Measurements

Conductances were measured in analytical grade dimethyl sulpoxide (DMSO) and dimethyl formamide (DMF) using dip type cell on Toshniwal Conductivity Bridge at the department of chemistry, Atarra P.G. College, Atarra.

### (ii) Magnetic measurements:

Room temperature magnetic susceptibility measurements of the investigated complexes were made by Gouy's method. Cobalt mercury thiocyanate was used as a calibrant.

### (iii) Infrared spectra measurements:

Infrared spectra (4000-450 $cm^{-1}$) of the uncoordinated ligands and synthesized complexes were recorded in nujol mulls supported between KBr pellets on Perkin Elmer (RXI) spectrometer (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

### (iv) UV-VIS spectral measurements

UV-VIS spectra of the uncoordinated ligands and synthesized complexes were recorded on Perkin Elmer lambda 15 UV-VIS spectrophotometer ranging from (260-700 nm) (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

### (v) NMR measurements

NMR spectra of the uncoordinated ligands and synthesized complexes were recorded on Brucker DRX-300MHz FT NMR using DMSO as solvent.

### (vi) Molecular weight determination

Molecular weight determination of the synthesized complexes were made by Rast's method.

## 3.3 PREPARATION OF THE PARENT COMPOUND

Potassium pentacynonitrocylchromate(I) monohy– drate was prepared by the method reported by Wilkinson et. al. as follows:

Chromium trioxide ($CrO_3$) (7 gm.) was added to a cold saturated solution of KOH (20 gm.) with ice cooling. Saturated aqueous KCN (35 gm.) was then added and the mixture filtered. $NH_2OH.HCl$ (8 gm.) was added to the filtrate and the solution was heated on steam both for two hours, and then filtered and cooled, and the filtrate poured

with stirring into ethanol (95%, 25 ml.). The precipitate was dissolved in minimum quantity of water and the compound again precipitated with ethanol; on crystallization from water gave bright crystals. Compound was characterized by elemental analysis and IR spectroscopy.

The observed results are as follows:

| | *K (in %)* | *Cr (in %)* | *C (in %)* | *N (in %)* | *$H_2O$ (in %)* |
|---|---|---|---|---|---|
| Experimental | 33.8 | 15.8 | 18.05 | 24.5 | 5.1 |
| Calculated | 33.8 | 15.1 | 18.03 | 24.2 | 5.2 |

| I.R.; | $\nu(NO)^+$ | $\nu(CN)$ |
|---|---|---|
| Found (reported) | | Found |
| (reported) | | |
| 1645 vs (1645 vs) | | 2135 (2135 s) |
| | 2192 (2195 s) | |

## 3.4 PREPARATION OF COMPLEXES

### (a) Preparation of $[Cr(NO)(CN)_2(5\text{-F Url})_2(H_2O)]$

To a filtered aqueous solution of potassium salt of the pentacynonitrocylchromate(I) monohydrate (0.1M, 50 ml.), an aqueous acetic acid solution (10 ml, 1:1) of the 5–Fluoro uracil ligand (0.02M) was added with shaking. A coloured solid was precipitated on heating the mixture for 20 minutes over a hot plate at 80°C. The resulting yellow-brown mixture

was freed from the liberated HCN by passing a current of $CO_2$ for few hours. The precipitate was suction filtered, washed several times with 10% acetic acid and finally with water and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 3.2

**(b) Preparation of $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$**

To a filtered aqueous solution of potassium salt of the pentacynonitrocylchromate(I) monohydrate (0.1M, 50 ml.), an aqueous acetic acid solution (10 ml, 1:1) of the 5–methyl uracil ligand (0.02M) was added with shaking. A coloured solid was precipitated on heating the mixture for 20 minutes over a hot plate at 80°C. The resulting greenish-brown mixture was freed from the liberated HCN by passing a current of $CO_2$ for few hours. The precipitate was suction filtered, washed several times with 10% acetic acid and finally with water and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 3.2.

## 3.5 PROPERTIES OF COMPLEXES

All the complexes are coloured solids (see Table 3.3 for colours). They are stable in air. Solubilities of these complexes in different solvents are given in Table 3.4. The complexes are thermally stable and do not melt or

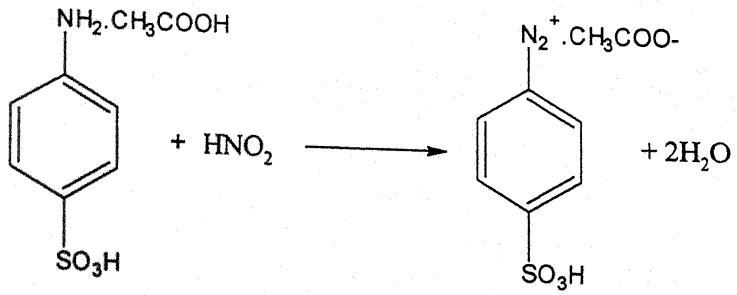
decompose upto 300°C (Table3.4). They decompose in dil. acids and alkalis only on heating. Both complexes after decomposition with KOH followed by acidifying with acetic acid give a pink coloured with few drops of Griess reagent **(29)**. This reaction indicates the presence of NO group in the synthesized complexes.

The probable reaction scheme for the Griess reagent is summarized as below.

## PROBABLE REACTION SCHEME FOR THE GRIESS REAGENT

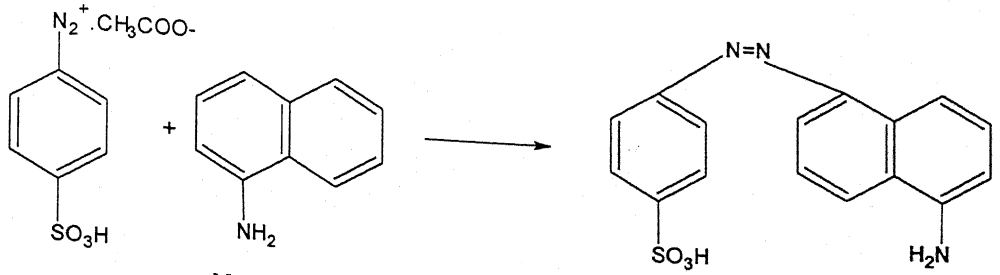
$$[Cr(NO)(CN)_2(L)_2(H_2O)] \xrightarrow[\text{Decomposition}]{KOH,\ H_2O} NO_2^- + \text{Chromium oxide}$$

$$NO_2^- + H^+ \longrightarrow HNO_2$$




Sulphanilic Acid

(A component of Griesss Reagent)




Naphthylamine

(Another component of Griess reagent)

Pink coloured dye + $CH_3COOH$

## 3.6 RESULTS AND DISCUSSION

The mixed-ligand cyanonitrosyl complexes (see Table 3.1 for ligand names) were prepared according to equation **(1).**

$$K_3[Cr(NO)(CN)_5].H_2O + 2L \xrightarrow[H_2O]{AcOH} [Cr(NO)(CN)_2(L)_2(H_2O)] + 3KOAC + 3HCN + H_2O$$

Where L = 5–Fluoro uracil and 5–methyl uracil

The partial replacement of cyano groups in the parent complex, $K_3[Cr(NO)(CN)_5.H_2O$ by two molecules of ligand, L, is facilitated by the trans effect of the NO group. Raynor and co-workers* studied the stepwise aqation of $[Cr(NO)(CN)_5]^{3-}$ and obtained the tris (aqua) species, $[Cr(NO)(CN)_5(H_2O)^3]$ which is consistent with equation **(1).**

Compounds were characterized by on the basis of following results:

### (a) Conductance Measurements

The molar conductance values measured in $10^{-3}$M dimethylsulphoxide as well as in dimethylformamide solutions. The conductance data are in agreement with the non-electrolytic nature **(8)** of these complexes.

**(b) Magnetic Measurements**

The magnetic moment values of the synthesized complexes at room temperature are presented in Table 3.7. An observation of the table shows that the magnetic moment values of the complexes are closed to the spin only values for one unpaired electron (1.73 B.M.)

**(c) Infrared Measurements**

The details of important infrared spectral bands of the synthesized complexes containing coordinated 5–Fluoro uracil and 5–methyl uracil with co-ordinated NO, CN are presented in table (3.8) respectively.

A comparison of the infrared spectra of the parent compound $K_3[Cr(NO)(CN)_5].H_2O$ and of the synthesized complexes suggests that the appearance of the very strong band in the region 1700-1710 $cm^{-1}$ in these complexes, is of coordinated $NO^+$ stretching. A positive shift of approximately 50 $cm^{-1}$ in these complexes compared to the parent compound indicates the non-electrolytic nature of these complexes.

Both of the synthesized compounds reported here show a strong band in the region 2140-2165 $cm^{-1}$. This band is assigned for ν(CN), which is good in agreement with other reported complexes.

The ligand 5–Fluoro uracil and 5–methyl uracil possesses 3 possible donor sites; **(i)** Two cyclic nitrogen cyclic nitrogen and **(ii)** oxygen of the ketonic group in ring

respectively. Out of these two the cycle nitrogen of ring system is supposed to be involved in coordination through the N atom. In the IR spectra of synthesized complex of 5–methyl uracil studied here, the IR frequency of cyclic nitrogen of ring has been changed, thereby, suggesting that the cyclic nitrogen has been participate in the coordination.

In the IR spectra of both the complexes with 5–methyl uracil the bands at 640 $cm^{-1}$ suffered a lower shift of 640 $cm^{-1}$, indicating the metal nitrogen coordination present in the synthesized compound. Hambright et al **(*465)** confirmed metal nitrogen co-ordination in the large series of complexes of Zn(II), Cu(II), Ni(II), Co(II) and Pt(II). Recently, Pannell and co-workers **(*472)** have experimentally confirmed the metal-nitrogen co-ordination in thiazole complexes.

The nitrile group may be involved in coordination through either the nitrogen or the triple bond. Coordination through nitrogen of the nitrile group invariably results in an increase in ν(CN) 32 by atleast 30 $cm^{-1}$.

The appearance of other broad bands in the range 3540-3570 $cm^{-1}$ and 3370-3400 $cm^{-1}$ in all the complexes is due to ν(OH) coordinated water(7).

The analytical data and all the evidences presented above suggest the formulation of these complexes as $[Cr(NO)(CN)_2(L)_2(H_2O)]$. Since all these synthesized complexes show one CN stretching band and one NO stretching band it is reasonable to propose an octahedral

structure **(10)** where CN is *trans* to CN and L *trans* to L and NO is *trans* to water in axial position.

## 3.7 SUMMARY

The novel mixed-ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium of the general formula $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (where L = 5–Fluoro uracil and 5–methyl uracil) have been prepared by the interaction of potassium pentacyanonitrosylchromate (I) monohydrate with the said ligands. The complexes, which have been characterized by elemental analysis, magnetic measurements, conductance studies, molecular weight determinations, infrared spectral studies, UV-VIS spectral analysis and NMR studies, contain chromium(I) in a low spin $\{CrNO\}^5$ electron configuration.

A suitable octahedral structure where CN is *trans* to CN and L is *trans* to L, and NO is *trans* to water is proposed for all the complexes. It is observed that –

**(i)** All the complexes are air stable coloured solids.

**(ii)** They are soluble in DMF, DMSO, ethanol and methanol but insoluble in nitrobenzene and ethyl acetate.

(iii) All the complexes contain $\{CrNO\}^5$ electron configuration.

(iv) All the compounds are thermally stable upto 300°C.

*(v)* All of them give pink colour with Griess Reagent.

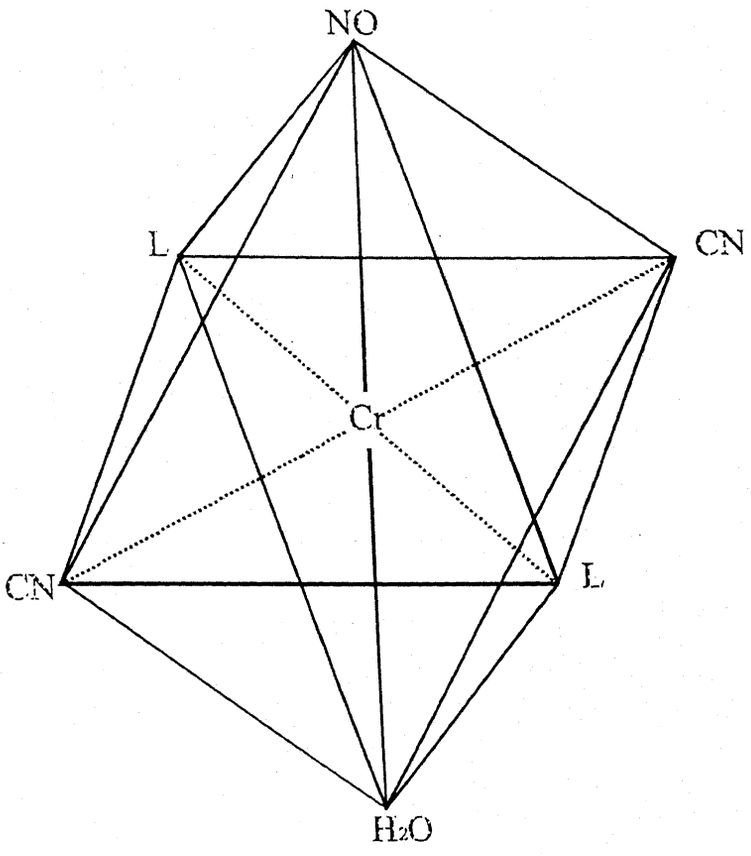
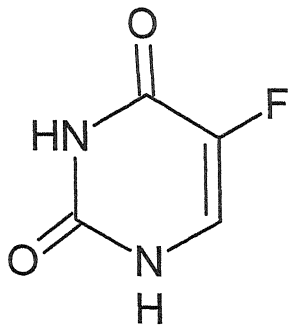
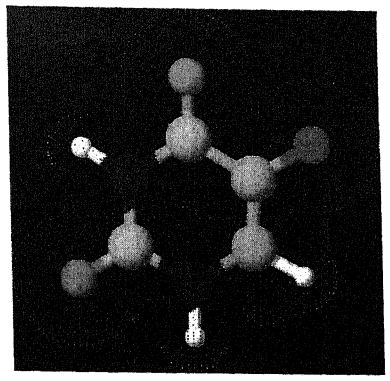


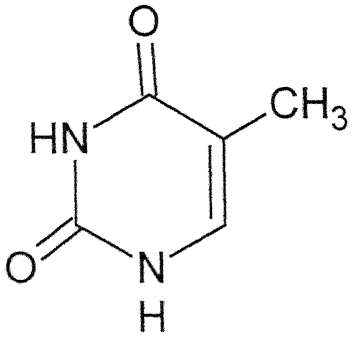

***Fig 3.1*** ***Proposed octahedral structure of*** $[Cr(NO)(CN)_2(L)_2(H_2O)]$

***(Where L = 5 – Fluoro uracil and 5- methyl uracil)***

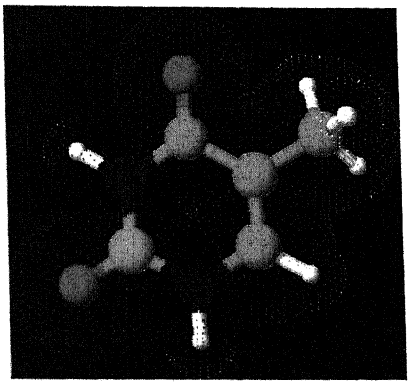



5-Fluorouracil






5-Methyluracil



## *Table 3.1*

## *I.U.P.A.C. Name and Electron Configuration of the synthesized complexes*

| *S. No.* | *Compound* | *I.U.P.A.C. Name* | *Electron Configuration* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | Aquadicyanodi(5–Fluoro uracil)-nitrosylchromium (I) | $\{CrNO\}^5$ |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | Aquadicyanodi(5–methyl uracil)-nitrosylchromium (I) | $\{CrNO\}^5$ |

## *Table 3.2*

## *Analytical Data of the Complexes*

| *S. No.* | *Compound* | *% Cr Found (Calc.)* | *% C Found (Calc.)* | *% H Found (Calc.)* | *% N Found (Calc.)* | *% S Found (Calc.)* |
|---|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | 10.34 (10.22) | 47.03 (47.23) | 4.58 (4.36) | 19.13 (19.28) | 12.32 (12.61) |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | 10.53 (10.14) | 42.54 (42.18) | 3.26 (3.54) | 19.04 (19.13) | 12.26 (12.51) |

## *Table 3.3*

## *Colour, Decomposition Temperature and % Yield of the Complexes*

| *S. No.* | *Compound* | *Colour* | *Decomposition Temperature (°C)* | *% Yield* |
|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | Yellow – brown | 300 | 45 |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | Greenish brown | 300 | 50 |

## *Table 3.4*

### *Solubilities of the Complexes in different Solvents*

| *S. No.* | *Compound* | *DMF* | *DMSO* | *EtOH* | *MeOH* | *Nitrobenzene* | *Ethylacetate* |
|---|---|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–}F\ Url)_2(H_2O)]$ | 55% | 55% | 30% | 20% | Insoluble | Insoluble |
| 2. | $[Cr(NO)(CN)_2(5\text{–}M\ Url)_2(H_2O)]$ | 50% | 60% | 35% | 25% | Insoluble | Insoluble |

## *Table 3.5*

### *Analytical Data of the Complexes*

| *S. No.* | *Compound* | *% Cr Found (Calc.)* | *% C Found (Calc.)* | *% H Found (Calc.)* | *% N Found (Calc.)* | *% F Found (Calc.)* |
|---|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | 12.42 (12.55) | 23.11 (23.20) | 1.45 (1.46) | 30.35 (30.44) | 9.15 (9.17) |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | 12.71 (12.80) | 29.49 (29.57) | 2.91 (2.98) | 30.89 (31.03) | – |

## *Table 3.6*

### *Dehydration temperature and molecular weight of the Complexes*

| *S. No.* | *Compound* | *Dehydration temperature (°C)* | *molecular weight)* | |
|---|---|---|---|---|
| | | | *Found* | *Calculated* |
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | 118 | 412.25 | 414.17 |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | 115 | 405.75 | 406.25 |

## *Table 3.7*

### *Magnetic and ESR data of the Complexes*

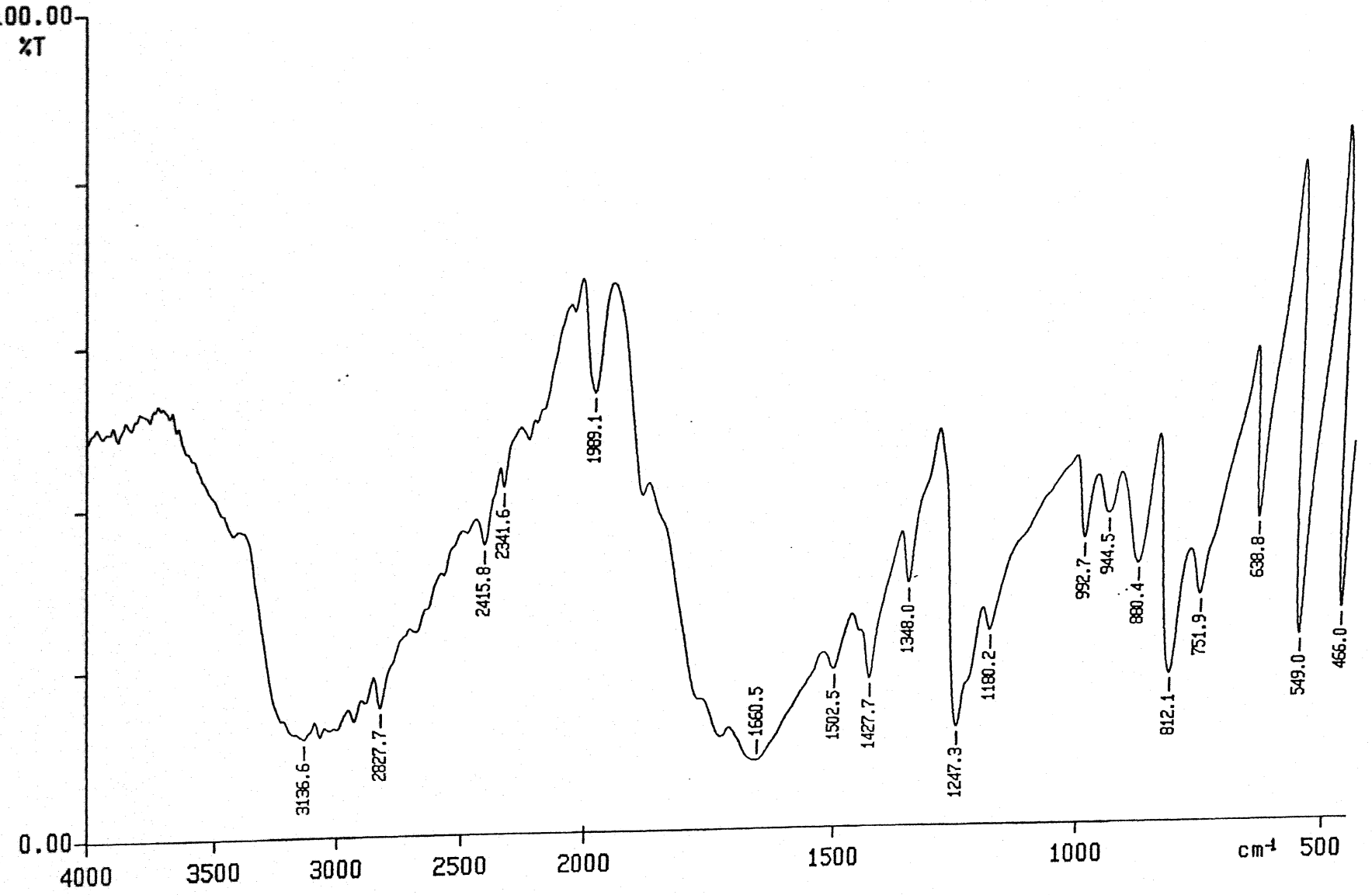
| *S. No.* | *Compound* | $\mu_{eff}$ | *'g'* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | 1.73 | 1.982 |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | 1.70 | 1.983 |

## *Table 3.8*

### *Important IR spectral bands and their assignments*

| S. No. | Compound | $\nu_{(NO)}^{+}$ | $\nu_{(CN)}$ | $\nu_{(NH)}$ | $\nu_{(OH)}$ |
|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(5\text{–F Url})_2(H_2O)]$ | 1710 | 2150 | 3275<br>3150 | 3575<br>3400 |
| 2. | $[Cr(NO)(CN)_2(5\text{–M Url})_2(H_2O)]$ | 1705 | 2160 | 3280<br>3160 | 3560<br>3410 |

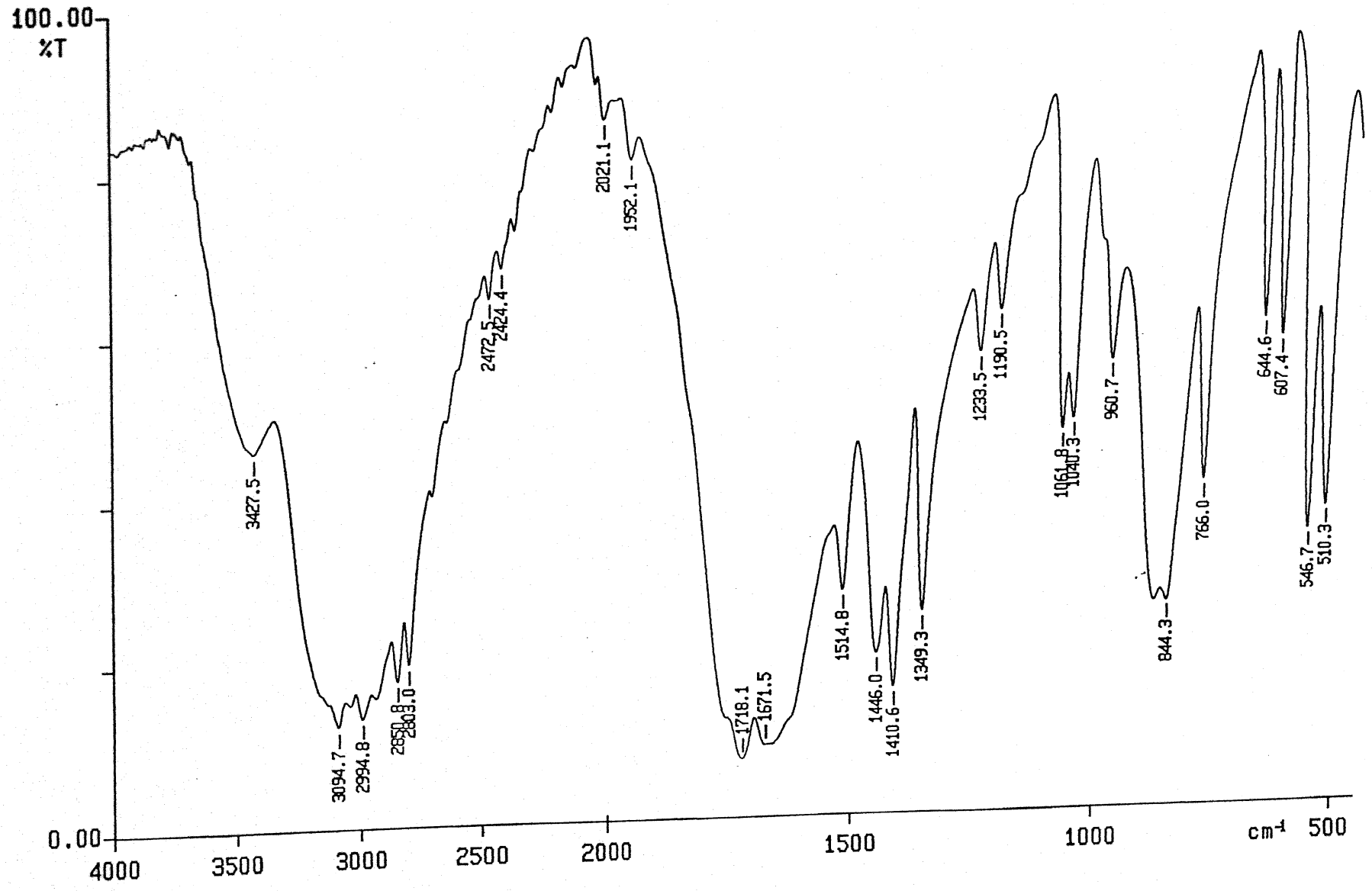
PERKIN ELMER




04/01/08 10:47 AH, CODE- B
X: 1 scan, 4.0cm-1, flat, smooth, abex

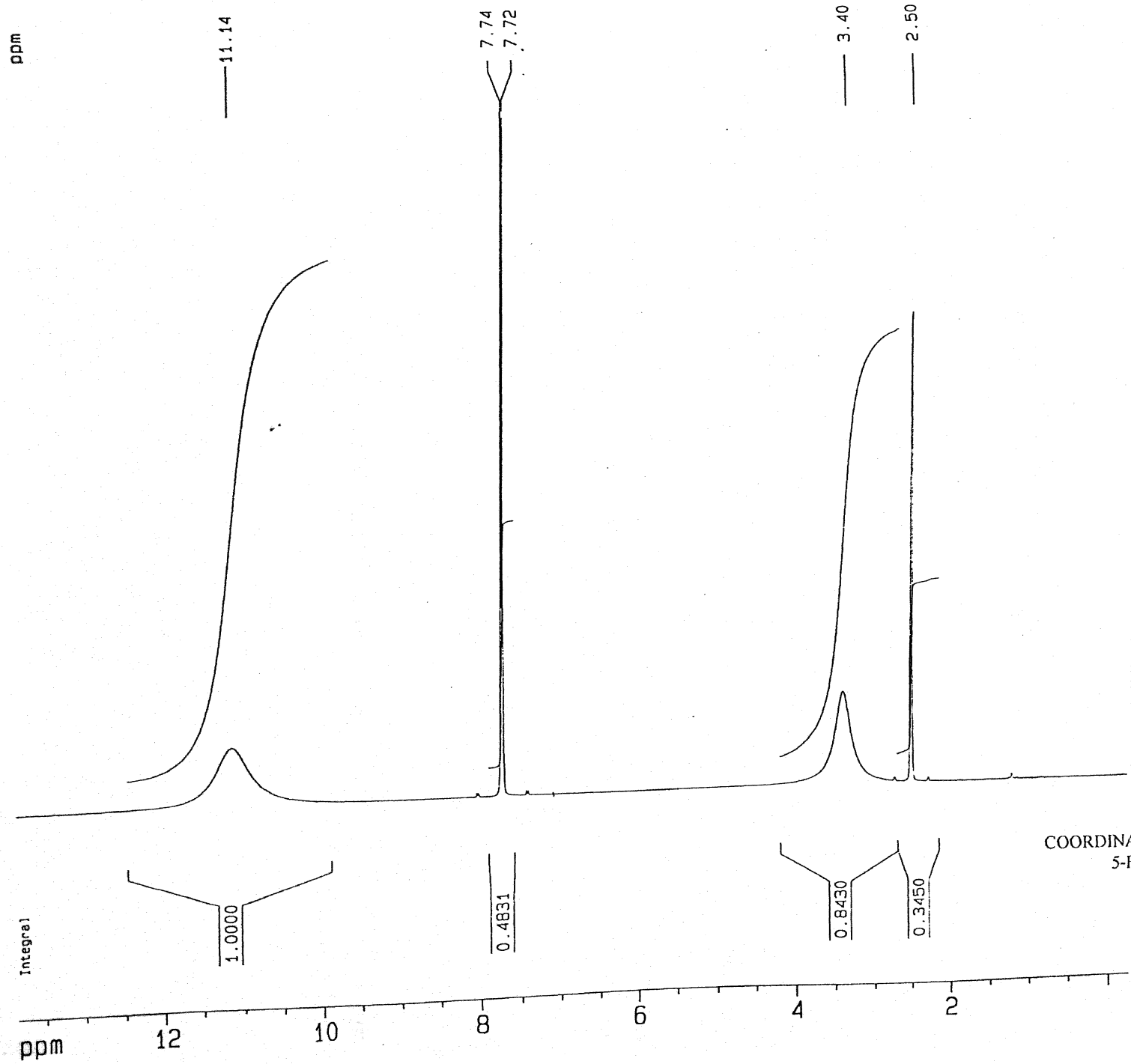
SAFF NO- 6809

**COORDINATION COMPOUND WITH 5-FLUORO URACIL**




04/01/08 10:51 AH, CODE- D
X: 4 scans, 4.0cm-1, flat, smooth, abex
SAIF NC - 6809

**COORDINATION COMPOUND WITH 5-METHYL URACIL**




Current Data Parameters

| | |
|---|---|
| NAME | 6809 b |
| EXPNO | 1 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20040303 |
| Time | 12.54 |
| INSTRUM | DRX300 |
| PROBHD | 5 mm Multinu |
| PULPROG | zg |
| TD | 32768 |
| SOLVENT | DMSO |
| NS | 16 |
| DS | 0 |
| SWH | 6680.556 Hz |
| FIDRES | 0.264910 Hz |
| AQ | 1.2374868 sec |
| RG | 101.6 |
| DW | 57.600 usec |
| DE | 6.00 usec |
| TE | 298.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 6.88 usec |
| PL1 | -3.00 dB |
| SFO1 | 300.1321300 MHz |

F2 - Processing parameters

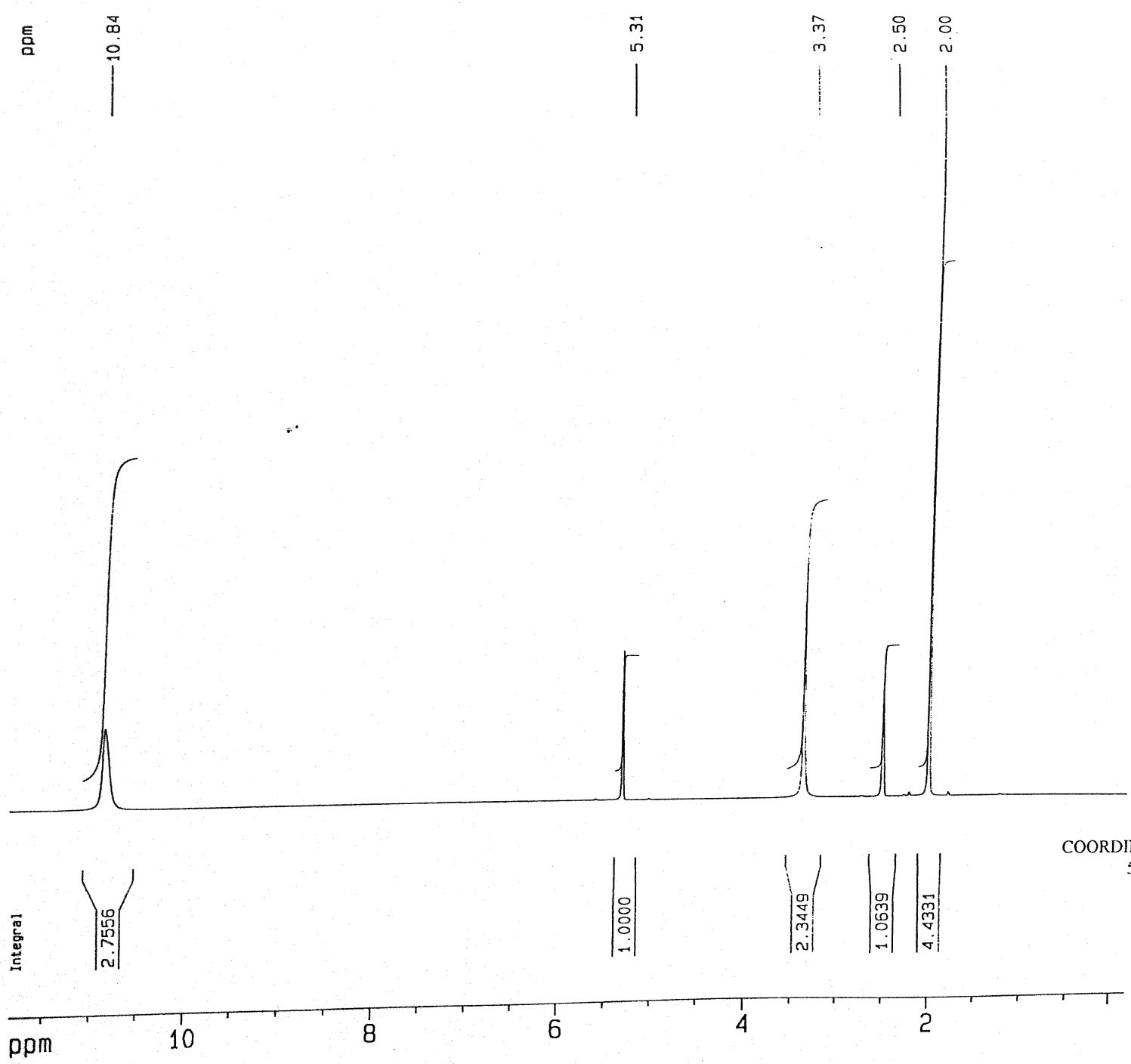
| | |
|---|---|
| SI | 16384 |
| SF | 300.1300010 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.10 Hz |
| GB | 0 |
| PC | 1.20 |

1D NMR plot parameters

| | |
|---|---|
| CX | 20.00 cm |
| F1P | 13.858 ppm |
| F1 | 4159.19 Hz |
| F2P | -0.266 ppm |
| F2 | -79.87 Hz |
| PPMCM | 0.70620 ppm/cm |
| HZCM | 211.95317 Hz/cm |

COORDINATION COMPOUND WITH
5-FLUORO URACIL

B
RSIC NO.6809




Current Data Parameters

| | |
|---|---|
| NAME | 6809.d |
| EXPNO | 1 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20040303 |
| Time | 12.38 |
| INSTRUM | DRX300 |
| PROBHD | 5 mm Multinu |
| PULPROG | zg |
| TD | 32768 |
| SOLVENT | DMSO |
| NS | 24 |
| DS | 0 |
| SWH | 8680.556 Hz |
| FIDRES | 0.264910 Hz |
| AQ | 1.8874668 sec |
| RG | 101.6 |
| DW | 57.600 usec |
| DE | 6.00 usec |
| TE | 298.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 6.88 usec |
| PL1 | -3.00 dB |
| SFO1 | 300.1321300 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 16384 |
| SF | 300.1300010 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.10 Hz |
| GB | 0 |
| PC | 1.20 |

1D NMR plot parameters

| | |
|---|---|
| CX | 20.00 cm |
| F1P | 11.835 ppm |
| F1 | 3551.91 Hz |
| F2P | -0.187 ppm |
| F2 | -56.06 Hz |
| PPMCM | 0.60107 ppm/cm |
| HZCM | 180.39836 Hz/cm |

COORDINATION COMPOUND WITH
5-METHYL URACIL

D

ASIC NO.6809

# Chapter IV

**Synthesis and physicochemical studies of new cyanonitrosyl $\{CrNO\}^5$ coordination compounds of Chromium with imidazole, 1-methyl imidazole and 2–methyl imidazole.**

# Chapter IV:

# Synthesis and physicochemical studies of new cyanonitrosyl $\{CrNO\}^5$ coordination compounds of Chromium with imidazole, 1-methyl imidazole and 2–methyl imidazole.

---

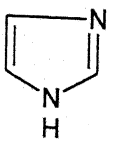
## 4.1 Introduction

In chapter III, synthesis and physiochemical studies of some mixed ligand cyanonitrosyl complexes of chromium having configuration $\{CrNO\}^5$ with some substituted benzothiazoles like 2-amino-5,6-dimethylbezothiazole and 2-Amino-4-methoxybezothiazole have been discussed. In continuation of our interest to synthesize and characterize some neutral mixed ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended using some substituted imidazoles.

In last few years, a great deal of interest has been shown to the study of neutral mixed-ligand cyanonitrosyl complexes of monovalent chromium **(4–8,10–14)**. Few attempts have been made by Maurya and coworkers to isolate some mixed ligand

cyanonitrosyl complexes of chromium having $\{CrNO\}^5$ electronic configuration with heterocyclic bases with one and two possible donor sites. It was, therefore, thought worthwhile to synthesize and characterize cyanonitrosyl complexes having $\{CrNO\}^5$ electronic configuration with some new heterocyclic compounds having more than one donor site like. Since this chapter involves the use of imidazole, 1-methyl imidazole and 2–methyl imidazole as a ligand so it will be better to discuss some important physico–chemical properties of imidazole derivatives.

Debus **(176)**, the discoverer of the parent compound, prepared it from glyoxal and ammonia and, to indicate its source, proposed the name glyoxaline. This name is still used in the modern literature especially by British workers. The name imidazole, used in the present monograph is due to Hantzsch**(177)**. He classified as azoles the five membered polyheteroatomic ring system containing at least one tertiary nitrogen. The term imidazole implies a five membered, heterocyclic ring system containing in addition to a tertiary nitrogen, an imino group; just as the names oxazole and thiazole designate five membered ring systems containing in addition to a tertiary nitrogen an oxygen or sulfur atom.




**Imidazole**

The correct numbering of the imidazole ring is shown above. The imino nitrogen receives position 1, and the numbering follows

around the ring so as to assign the smallest possible number to the tertiary nitrogen, which is designated as position 3. the substituted nitrogen represents the starting point for the numbering of the N-substituted imidazoles. The designation of a substituent in position 2 offers no problem because of the symmetrical location with respect to the nitrogens. The naming becomes somewhat more complex, however, when a substituent is introduced into the 4- or 5- position. Depending upon the position of the imino hydrogen such a compound must be designated as either a 4- or a 5-monosubstituted imidazole, the tautomeric character of the imidazoles precluding a definite assignment of structure. Such compounds are designated as 4(or 5)-monosubstituted imidazoles.

The presence in the imidazole structure of an acidic pyrrole nitrogen and a basic pyridine nitrogen explains the amphoteric nature of these compounds. Qualitatively, the imidazoles may be regarded as a "cross" between a pyridine and a pyrrole. Thus one could expect a deactivating influence toward electrophilic reagents caused by the pyridine nitrogen, which to a certain degree is offset by the electron-releasing properties of the pyrrole nitrogen. The chemical behavior of the imidazoles is in agreement with this admittedly crude picture.

The consideration of structure must be based on physical as well as chemical properties. It thus seems logical to summarize first the physical properties of the imidazoles. Whenever possible, this done from the point of view of comparison, since pertinent

information on other heterocyclic ring systems will aid in understanding the imidazole problem.

### (i) Boiling Point

**TABLE I.**

**Boiling Points Of A Number Of Five-Membered Heterocyclic compounds**

| COMPOUNDS | B.p., $^{0}$C. (760mm.) |
|---|---|
| Furan | 32 |
| Pyrrole | 131 |
| Pyrazole | 187 |
| Imidazole | 256 |

Table I summarizes the boiling points of a number of five membered heterocyclic compounds and illustrates the unusually high boiling points of imidazole. Pyrazole also boils rather high in comparison with furan, and pyrrole, although it does not differ significantly from them in molecular weight.

The boiling point of imidazole is strikingly lowered by the introduction of a methyl group in to the 1-position, but is not significantly affected by the introduction of a methyl group in to the 4(or 5) –position. Even the introduction of an amyl group, which doubles the molecular weight, results in a substance boiling lower than the parent ring system. These results demonstrate that the free imino hydrogen is, to a certain degree, responsible for the observed high boiling points of imidazoles (table II)

**Table- II**

***Effect of substituents ontheboiling point of imidazole***

| compounds | B.p., $^0$C.(760mm.) |
|---|---|
| Imidazole | 256 |
| 1-Methyl | 198 |
| 4(or 5)Methyl | 264 |
| 1-Propyl | 223 |
| 1-Amyl | 245 |
| 1,2-Dimethyl | 205 |
| 1-Ethyl-2-Methyl | 211 |
| 1-Methyl-5-Chloro | 202 |
| 1-Methyl-4-Chloro | 245 |
| 1,4-Dimethyl | 200 |
| 1,5-Dimethyl | 220 |
| 1-Phenyl | 277 |
| 2-Phenyl | 340 |

## 2. Melting points

Table III summarizes the melting points of a number of imidazoles. Here again it will be noted that the introduction of a substituents into the 1-position of the imidazole ring has a striking lowering effect.

## Table III

### *Melting points of a number of Imidazole*

| Compounds | M.p., $^0$C |
|---|---|
| Imidazole | 90 |
| 1-Methyl | -6 |
| 2-Methyl | 140-141 |
| 4(or 5)-Methyl | 55-56 |
| 1-Phenyl | 13 |
| 2-Phenyl | 148-149 |
| 4(or 5)-phenyl | 133-134 |
| 1-Benzyl | 71-72 |
| 2-Benzyl | 125-126 |
| 4(or 5)-Benzyl | 82-84 |
| 4,5-Diphenyl | 228 |
| 2-Methyl-4,5-diphenyl | 240 |
| 1-Methyl-4,5-diphenyl | 158 |

## 3. Solubility

The solubility of imidazole is high in polar and low in non-polar solvents. At room temperature is so extremely soluble in waterthat quantitative data on its solubility have not been obtained. The base is somewhat soluble in benzene; however, at room temp. its solubility in this solvent is rather limited. Cyclohexane is poor solvent. 4(or 5)-Methylimidazole exhibits good solubility in benzene. The N-substituted imidazoles are in general much more soluble in non polar solvents than are the imidazoles with a free imino hydrogen. Quantitative figures on the solublities of imidazole in benzene and in dioxane, and of 4(or 5)-methyl imidazole in benzene are given in table IV and V.

**Table IV.**

***Solubility of Imidazole in Benzene and in Dioxane (3)***

| Benzene | | Dioxane | |
|---|---|---|---|
| Temp.,$^0$C, | Molality | Temp.,$^0$C, | Molality |
| 36.7 | 0.198 | 14.7 | 3.62 |
| 41.0 | 0.258 | 17.9 | 4.29 |
| 42.2 | 0.486 | 21.9 | 4.96 |
| 42.8 | 0.688 | 23.0 | 5.17 |
| 44.8 | 1.195 | 32.7 | 7.48 |
| 45.7 | 1.524 | 38.0 | 9.46 |
| 17.8 | 2.38 | 39.4 | 10.5 |
| 49.0 | 3.00 | 46.8 | 14.2 |
| 51.2 | 4.63 | 55.8 | 19.3 |

**Table V.**

***Solubility of 4(or 5)-Methylimidazole in Benzene (3)***

| Temperature, $^0$C. | Molality |
|---|---|
| 3.2 | 4.57 |
| 16.8 | 6.07 |
| 21.1 | 6.87 |
| 25.4 | 7.44 |
| 29.3 | 8.24 |
| 31.4 | 8.54 |

## 4. Molecular Weight and Degree of Association

Ebulliometric molecular weight determinations in boiling benzene also yield abnormal results. For example, 4(or 5)-methylimidazole at a concentration of 0.4 m exhibits an apparent molecular weight of 190, which is approximately twice the formula weight. Imidazole is also appreciably associated in boiling benzene, since at a concentration of 0.4 m a molecular weight of 250 is observed (approximately four times the formula weight). It is of interest to note that imidazole in aqueous solution exhibits a normal molecular weight which changes little with increasing concentration.

All these finding points to a high degree of association of the imidazoles in non polar solvents; that the association is dependent on the presence of a free imino hydrogen is evidenced by the low degree of association of the N-substituted imidazoles and benzimidazoles.

## 5. Viscosity

The specific viscosity of benzene solutions of imidazole and 4 (or 5)-methylimidazole are given in table-VI. Solution of pyrazole in benzene have approximately the same viscosity as the pure solvent, and neligible variation of the specific viscosity with increasing concentration is observed. This suggests little association. The specific viscosity of solution of imidazole and 4 (or 5) –methylimidazole, on the other hand, increases with increasing concentration (see table VI), a behavior pointing to the presence of long chain aggregates.

## Table VI

*Viscosity of Benzene Solution of Imidazole and 4(or 5)-Methylimidazole*

| Compound (temp., $^0$C.) | Molality | Specific visccosity |
|---|---|---|
| Imidazole (30 $^0$)..... | 0.036 | 0.0106 |
| | 0.073 | 0.0248 |
| | 0.146 | 0.0549 |
| Imidazole (50 $^0$)..... | 0.146 | 0.0410 |
| | 0.461 | 0.1500 |
| | 0.463 | 0.1686 |
| 4(or 5)-Methylimidazole (30 $^0$).... | 0.040 | 0.0071 |
| | 0.080 | 0.0354 |
| | 0.242 | 0.1187 |
| | 0.249 | 0.1277 |
| | 0.475 | 0.2925 |
| | 0.493 | 0.3262 |
| | 0.607 | 0.4113 |
| | 1.075 | 0.7801 |
| | 1.362 | 0.991 |
| | 2.068 | 1.6524 |
| | 2.848 | 2.3138 |
| | 3.738 | 3.1560 |
| 4 (or 5)-Methylimidazole (50 $^0$)... | 0.242 | 0.0910 |
| | 0.249 | 0.0930 |
| | 0.475 | 0.2140 |
| | 0.493 | 0.2370 |

## 6. Dipole Moments

Most valuable information on the fine structure of organic molecules may be gained from an exact knowledge of their dielectric properties, since the magnitude of the dipole moments is indicative of the charge distribution within their structures. Unfortunately the experimental material on imidazoles is rather limited, dipole moments being available only for imidazole, 4(or 5)-methylimidazole, 1-methylimidazole, and benzimidazole. The results are summarized in table VII.

**Table VII.**

***Diploe Moment in Debye Units of Some Imidazoles in Different Solvents (3,7)***

| Compound | Naphthalene | Benzene | Dioxane | Carbon tetra chloride |
|---|---|---|---|---|
| Imidazole..... | 5.7 ((97 $^0$) | 6.2(70 $^0$) | 4.8 (30 $^0$) | - |
| 4(or 5)-Methyl..... | - | 6.2(70 $^0$) | 5.1(20 $^0$) | 5.8(18 $^0$) |
| 1-Methyl..... | - | 3.6(20 $^0$) | 3.8(20 $^0$) | - |
| Imidazole*..... | - | 3.8 | - | - |

*Infinite dilution.

Again the high degree of associtation of the imidazoles containing a free imino group in nonpolar solvents reflects itself in the dipole moments. Thus the moment of 1-methylimidazole when measured in benzene solution is little dependent on the concentration, in contrast to that of imidazole which varies to a considerable extent as illustrated in table VIII.

Table VIII.

*Variation (with Concentration) of the Dipole Moment of Imidazole in Benzene (7)*

| Mole fraction of solute | Dipole moment,Debye unit |
|---|---|
| 0.005951 | 5.62 |
| 0.001140 | 4.42 |
| 0.000233 | 3.93 |

## 7. Spectroscopic Properties

### *(a) Ultraviolet Absorption Spectra*

The simple imidazoles fail to exhibit selective absorption in the ultraviolet region **(8,9)**. Selective absorption is observed in imidazoles in which imidazole ring is conjugated with a carbonyl group, such as in the imidazolecarboxaldehydes and imidazolecarboxylic acids. Also certain functional derivatives such as the imidazolethiones exhibits charactersic absorption maxima in the ultraviolet region. The spectra of these compounds will be found in the appropriate sections.

### *(b) Raman Spectra*

The Raman spectra of various imidazoles have been investigated, and the reader is referred to the original literature on this subject **(10)**.

### *(c) Chemiluminescence*

A number of arylimidazoles exhibit chemiluminescence when exposed to the action of an oxidizing reagent in alkaline medium. This interesting phenomenon was first observed by

Radziszewski **(11)** who found that a solution of 2,4,5-triphenylimidazole (lophine) in potassium hydroxide emitted light when it was shaken with air. He was struck by the intense light production and described his observation as follows: "the phenomenon becomes rather spectacular on a large scale; I employed 100 g. of lophine and 300 g. of potassium hydroxide in alcohol for my experiments. The development of light was so intense that it was possible to see the faces of the observers at a distance of two or three feet and at a distance of two and one half to five cm. the numbers and hands of a pocket was could be recognized".

The addition of an oxidizing agents to a solution of lophine an alkali brings about a marked increase of the chemiluminescence. Optimal effects are obtained when a solution of lophine in ethanol, methanol, acetone or dioxane is treated with an oxidizing reagentssuch as hypohalite, potassium ferricyanide, hydrogen peroxide, or hemoglobin **(12-15)**. A variety of substituted aryl imidazoles such as 2,4,5-tri(p-methylphenyl)-, 2,4,5-tris(p-methoxyphenyl)-, and 2,4,5- tris (p-chlorophenyl)-imidazole, or substances like 4,5-diphenyl-2-methyl-, 4,5-diphenyl-2-ethyl-, 4,5-diphenyl-2-isopropyl-, and 4,5-diphenyl-2-(p-methoxyphenyl)-imidazole exhibit chemiluminescence under the above mentioned conditions **(16)**. Amarine (2,4,5-triphenyl-2-imidazoline) behaves similarily **(14)**. Imidazole exhibits a weak degree of chemiluminescence upon exposure to hydrogen peroxide **(12)**.

The emited light exhibits a continuous spectrum ranging from 4800-6000 A, with a maximum at 5300 A.

## 8. Miscellaneous Physical Properties

Information on refractive indexes, densities, molar refractivities, surface tensions, heat of fusion, and heats of solution of imidazole and 4(or 5)-methylimidazole is summarized in table IX, X.

**Table IX.** ***Suyrface Tension of Imidazole and 4(or 5)-Methylimidazole (3)***

| **Compound** | **Temperature, $^0$C.** | **Surface tension,dynes/cm.** |
|---|---|---|
| Imidazole ..... | 110.0 | 36.82 |
| | 150.0 | 33.85 |
| | 205.0 | 30.05 |
| 4(or 5)-Methyl-..... | 20.0 | 38.70 |
| | 56.0 | 36.21 |
| | 110.0 | 32.36 |
| | 153.0 | 29.28 |

**Table X.**

***Heat Of Fusion And Heat Of Solution In Benzene At Varying***

| Molality | Heat of solution, cal./mole ($21^0$) | Heat of fusion. cal/mole |
|---|---|---|
| 0.13 | -3210 | -2840 |
| 0.22 | -2170 | - |

***Concentration Of 4(Or 5)-Methyl, Imidazole (3)***

## 9. Chemical Properties

### 1. Basic Strength

Imidazole is a monoacidic base have the ability to form crystalline salts with acids. The melting points of a number of characteristic imidazolium salts are listed in table XI. The basic nature of the imidazoles is due to the ability of the pyridine nitrogen to accept a proton.

Substituents influence the basic strength of imidazole in the manner illustrated in table XII. The introduction of methyl groups into the imidazole ring increases its basic strength. This is applicable in terms of the electron-releasing properties of the methyl group, which tends to increase the electron density about the pyridine nitrogen. The situation parallels that observed in the pyridine series, where the basic strength of α-picoline is also higher than that of the parent ring system **(33)**. This increase in basic strength has been attributed to combine inductive and resonance effect (hyperconjugation).

methylimidazole, where hyperconjugated states of the type depicted below are indicated. The introduction of a methyl group into the 4(or 5)- position of the imidazole ring also increases the basic strength, but the effect is less pronounced than that of the 2-methyl group symmetry considerations might offer an explanation for this difference. The 2-methylimidazolium ion represents a highly symmetrical structure with two equivalent contributions, in contrast to the 4(or 5)-methylimidazolium ion with two non-equivalent contributions. The introduction of a methyl group into both the 2- and the 4(or 5)-position causes a further increase in basic strength.

**Table XI.**

***Melting Points of a Number of Imidazole Salts***

| Salts | M.p., $^0$C. | References |
|---|---|---|
| Nitrate ..... | 118 | (30) |
| Chloroaurate..... | dec. 190 | (29) |
| Chloroplatinate..... | dec. 200 | (31) |
| Dimolibdate..... | | (27,28) |
| Picrate..... | 208-212 | (20,22-24) |
| Flavinate..... | 224-226 | (26) |
| Diliturate..... | | (25) |
| Acid oxalate..... | 232,252,225 | (20-23) |
| Acid tartrate..... | 202 | (22) |
| Benzoate..... | 99 | (18,19) |

Electron-attracting groups such as the phenyl group, the nitro group, or a halogen, decrease the basic strength. A few qualitative observation on the basic strength of N-alkylnitroimidazoles are of interest. A comparison of 1-methyl-5-nitroimidazole and 1,2-di-methyl-5-nitroimidazole with their respective 4-nitro derivatives indicates that the 5-nitro compounds are the stronger bases **(178, 179)**. It seems logical that the structure in which the nitro group is located in close proximity to the electron-donor system (pyridine nitrogen ) should represent the weaker base.

Table XII.

***Basic strength of a number of imidazoles (30,32,32a)***

| compounds | pKα |
|---|---|
| Imidazole | 6.95;6.89[a] |
| 1-methyl | 7.25 |
| 2-methyl | 7.86 |
| 4(or 5)-methyl | 7.52 |
| 2,4(or 2,5)-dimethyl- | 8.36 |
| 2,4,5-trimethyl- | 8.86[a] |
| 2-phenyl- | 6.39 |
| 4(or 5)-phenyl)- | 6.00 |
| 4(or 5)-hydroxymethyl- | 6.38 |
| 4(or 5)-carboxy- | 6.08[a] |
| 4(or 5)-carbethoxy | 3.66[a] |
| 4(or 5)-bromo- | 3.60[a] |
| Histamine | 5.98[a] |

## 2. Pseudoacidic Character

In addition to its basic nature, imidazole also exhibits weakly acidic(pseudoacidic) properties. It forms salts with metals of the general structure shown below. Most important among the salts is the sparingly soluble silver salt, which is precipitated when imidazole is brought into contact with ammoniacal silvar solutions. In the presence of ammonia, in soluble salts with cobalt and zinc are also obtained **(180, 181)**. The reaction of imidazole with a Grignard reagent results in the formation of an imidazole magnesium halide **(182, 183)**.

The pseudoacidic nature of imidazole depends upon the presence of the unsubstituted imino group, and imidazoles having this structural requirement form sparingly soluble silver salts in the presence of ammoniacal silver solutions. Many imidazoles form insoluble salts with cuprous ion in the presence of ammonia **(184)**. Imidazole dissolves in liquid ammonia, forming a clear solution from which it is regenerated on evaporation of the solvent. The addition metals or of metal amides to such a solution result in salt formation. The sodoium, potassium, calcium, and magnesiumsalts obtained in this manner. These salts are unstable in the presence of water and hydrolyze with the formation of imidazole and metallic hydroxides **(185)**. A comparison of the conductance of liquid ammonia solutions of imidazole and of pyrrole demonstrates the former compounds to represent the stronger acid. Electronegative substituents increase the acidic properties of the imidazoles by decreasing the electron density about the pyrrole nitrogen.

Lophine is a stronger acid than imidazole. Like imidazole,lophine forms salts upon treatment with metals or metal amides in liquid ammonia solution **(186)**.

2,4,5-tribromoimidazole is strong enough acid to dissolve in aqueous sodium carbonate solution **(187)**.

### 3. Chemical Stability And Aromatic Character

Although a detailed discussion of the chemical behaviour of the imidazoles will represent the subject of later chapters, it seems pertinent to summarize briefly a number of their key properties prior to consideration of structure.

Outstanding is the pronounced chemical stability of the imidazoles. They are resistant to the most drastic treatments with acids and bases. Exposers of imidazoles to the action of the iodide at temperatures up to $300^0$ has little effect, and the imidazole ring resist catalytic hydrogenation to a remarkable degree. A number of benzimidazoles, such as 2-methyl, 2-ethyl, and 1,2-dimethyl-benzimidazole, in the presence of Adams catalyst and glacial acetic acid undergo hydrogenation in the benzene portion with the formation of the corresponding tetrahydro derivatives. The imidazole portion remains unaffected.

Imidazole is stable toward chromium trioxide **(187)**, but is readily attacked by potassium permagnate and hydrogen peroxide with the formation of oxamide **(188, 189)**. Benzoyl peroxide in chloroform solution also attacks imidazole readily with formation of urea and ammonia **(190)**.

## 4.2 EXPERIMNTAL

### *(a) Materials employed:*

Imidazole and 1-methyl imidazole and 2–methyl imidazole were obtained from Aldrich Chemical Company,

USA. Hydroxylaminehydrochloride and Chromic acid were supplied by SD Fine Mumbai. Potassium Cyanide was procured from May and Baker Limited, Dagenham. Distilled water was used in all the operations.

*(b) Analysis of the constituent elements:*

(i) Carbon, hydrogen and nitrogen were estimated micro-analytically.

(ii) **Estimation of chromium:**

For the estimation of the chromium as chromic oxide ($Cr_2O_3$), the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. chromium was precipitated as chromic hydroxide by means of dil. ammonium hydroxide. chromic hydroxide, when ignited, was converted into $Cr_2O_3$. Repeated heating, cooling and weighing were carried out until constant weight obtained.

*(c) Physical Methods:*

(i) **Conductance Measurements**

Conductances were measured in analytical grade dimethyl sulpoxide (DMSO) and dimethyl formamide (DMF) using dip type cell on Toshniwal Conductivity Bridge at the department of chemistry, Atarra P.G. College, Atarra.

**(ii) Magnetic measurements:**

Magnetic susceptibility measurements of the ynthesized complexes were made by Gouy's method. Cobalt mercury thiocyanate was used as a calibrant.

**(iii) Infrared spectra measurements:**

Infrared spectra (4000-450 $cm^{-1}$) of the uncoordinated ligands and synthesized complexes were recorded in nujol mulls supported between KBr pellets on Perkin Elmer (RXI) spectrometer (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

**(iv) UV-VIS spectral measurements**

UV-VIS spectra of the uncoordinated ligands and synthesized complexes were recorded on Perkin Elmer lambda 15 UV-VIS spectrophotometer ranging from (260-700 nm) (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

**(v) NMR measurements**

NMR spectra of the uncoordinated ligands and synthesized complexes were recorded on Brucker DRX-300MHz FT NMR using DMSO as solvent.

(vi) **Molecular weight determination**

Molecular weight determination of the synthesized complexes were made by Rast's method.

## 4.3 PREPARATION OF THE PARENT COMPOUND

Potassium pentacynonitrocylchromate(I) monohydrate $K_3[Cr(NO)\ (CN)_5].H_2O$ was again used as the parent compound for synthesizing the complexes under this investigation.

## 4.4 PREPARATION OF COMPLEXES

### (a) Preparation of $[Cr(NO)(CN)_2(IMD)_2(H_2O)]$

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacynonitrocylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the imidazole ligand (0.02M) was added with shaking. When a brownish-greenish coloured solid was precipitated on warming the mixture for 20 minutes over a hot plate at 80°C., the resulting mixture was freed from the liberated HCN by passing a current of $CO_2$ for few hours. The precipitate was filtered, washed several times with water and finally with ethanol and ether and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 4.2

### (b) Preparation of $[Cr(NO)(CN)_2(1\text{–}M\ Imd)_2(H_2O)]$

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacynonitrocylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of

the 1-methyl imidazole (0.02M) was added with shaking. When a greenish-yellow coloured solid was precipitated on warming the mixture for 20 minutes over a hot plate at 80°C., the resulting mixture was freed from the liberated HCN by passing a current of $CO_2$ for few hours. The precipitate was filtered, washed several times with water and finally with ethanol and ether and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 4.2.

**(c) Preparation of $[Cr(NO)(CN)_2(2\text{–M Imd})_2(H_2O)]$**

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacynonitrocylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the 2-methyl imidazole (0.02M) was added with shaking. When a yellowish-brown coloured solid was precipitated on warming the mixture for 20 minutes over a hot plate at 80°C., the resulting mixture was freed from the liberated HCN by passing a current of $CO_2$ for few hours. The precipitate was filtered, washed several times with water and finally with ethanol and ether and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 4.2

## 4.5 PROPERTIES OF COMPLEXES

All the complexes are coloured solids (see Table 4.3 for colours). They are stable in air. Solubilities of these complexes in different solvents are given in Table 4.4. The

complexes are thermally stable and do not melt or decompose upto 260°C (Table 4.3).They decompose in dil. acids and alkalis only on heating. Both complexes after decomposition with KOH followed by acidifying with acetic acid give a pink coloured with few drops of Griess reagent(**29**). This reaction indicates the presence of NO group in the synthesized complexes.

## 4.6 RESULTS AND DISCUSSION

The mixed-ligand cyanonitrosyl complexes (see Table 4.1 for ligand names) were synthesized according to equation (**1**).

$$K_3[Cr(NO)(CN)_5].H_2O + 2L \xrightarrow[H_2O]{AcOH} [Cr(NO)(CN)_2(L)_2(H_2O)] + 3KOAC + 3HCN + H_2O$$

Where L = Imidazole, 1-methyl imidazole and 2–methyl imidazole

The partial replacement of cyano groups in the hexa co-ordinated complexes, $K_3[Cr(NO)(CN)_5].H_2O$ by two molecules of ligand, L, arises from the trans effect of the NO group. Studies of Raynor and co-workers on stepwise aquation of the pentacyanonitrosylchromate(I) $[Cr(NO)(CN)_5]^{3-}$ to attain $[Cr(NO)(CN)_2(H_2O)_3]$ favour the above reaction scheme.

Compounds were characterized by on the basis of following results:

**(a) Conductance Measurements**

The molar conductance values measured in $10^{-3}$M dimethylsulphoxide as well as in dimethylformamide solutions for these complexes are presented in Table 4.5. The conductance data are in agreement with the non-electrolytic nature **(8)** of these complexes.

**(b) Magnetic Measurements**

The magnetic moment values of the synthesized complexes at room temperature are presented in Table 4.7. An observation of the table shows that the magnetic moment values of the complexes are closed to the spin only values for one unpaired electron (1.73 B.M.)

**(c) Infrared spectral studies**

The important IR spectral bands of the synthesized complexes containing coordinated Imidazole, 1-methyl imidazole and 2–methyl imidazole with other ligands are presented in table 4.8 respectively.

The ligand imidazole, 1-methyl imidazole and 2–methyl imidazole possess 2 possible donor sites; two cyclic nitrogen ring system. Further that the cyclic nitrogen atom involved in coordination through the N atom. The IR frequency of tertiary cyclic nitrogen ring is and essentially changed, thereby, suggesting the cyclic nitrogen of this ligand participate in the coordination.

Coordination through the ring nitrogen present in the imidazole ring causes an increase in the ring ν(CN) and imidazole ring breathing mode. In the uncoordinated ligand, the imidazole ring breathing mode appears at 1329 $cm^{-1}$. The significant positive shift for imidazole ring breathing mode in the synthesized complex with imidazole indicates conclusively that coordination of the ligand takes place through imidazole ring nitrogen only.

Both the synthesized complexes exhibit a broad band in the region 3580–3550 $cm^{-1}$ indicating the presence of ν(OH) of the coordinated water. The synthesized complexes also show a strong band in the region 2120-2150 $cm^{-1}$ which may be assigned for ν(CN), which is in accordance with assignment made for other reported complexes.

The analytical data and all the evidences presented above suggest the formulation of these complexes as $[Cr(NO)(CN)_2(L)_2(H_2O)]$. Since all these complexes show one CN stretching band and one NO stretching band it is reasonable to propose an octahedral structure **(10)** where CN is *trans* to CN and L ligands are *trans* to each other in equatorial position, whereas NO is *trans* to water in axial position.

## 4.7 SUMMARY

The novel mixed-ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium of the general formula $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (where L = imidazole, 1-methly imidazole and 2–methyl imidazole )

have been prepared by the interaction of potassium pentacyanonitrosylchromate(I)monohydrate with the said ligands. The complexes, which have been characterized by elemental analysis, magnetic measurements, conductance studies, molecular weight determinations, infrared spectral studies, UV-VIS spectral analysis and NMR studies, contain chromium(I) in a low spin $\{CrNO\}^5$ electron configuration.

A suitable octahedral structure where CN is *trans* to CN and L is *trans* to L, and NO is *trans* to water is proposed for all the complexes. It is observed that –

**(i)** All the complexes are air stable coloured solids

**(ii)** They are soluble in DMF, DMSO, ethanol and methanol but insoluble in nitrobenzene and ethyl acetate.

**(ii)** All the complexes contain $\{CrNO\}^5$ electron configuration.

**(iv)** All the compounds are thermally stable upto 300°C.

***(v)*** All of them give pink colour with Griess Reagent.

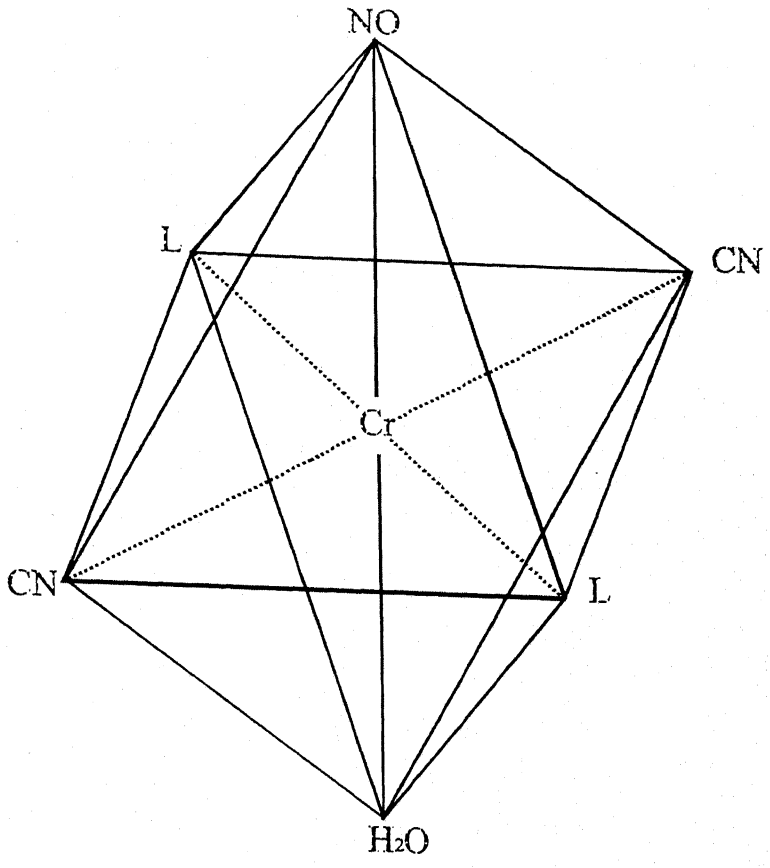
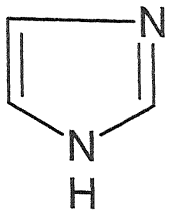
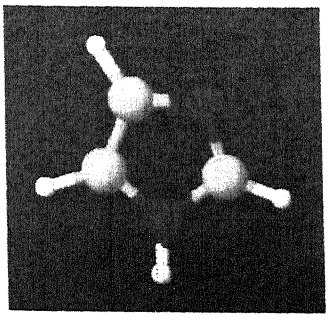
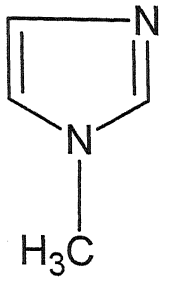



*Fig 4.1* ***Proposed octahedral structure of*** $[Cr(NO)(CN)_2(L)_2(H_2O)]$
***(where L = imidazole, 1-methly imidazole and 2–methyl imidazole)***

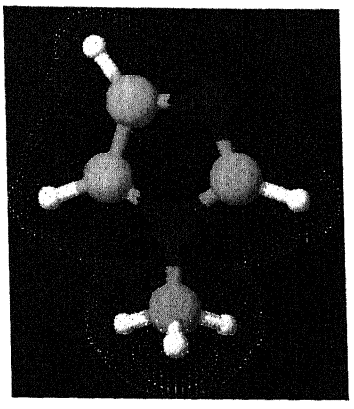


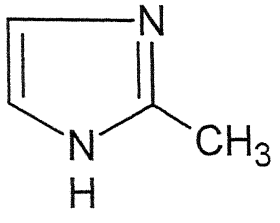

1*H*-imidazole



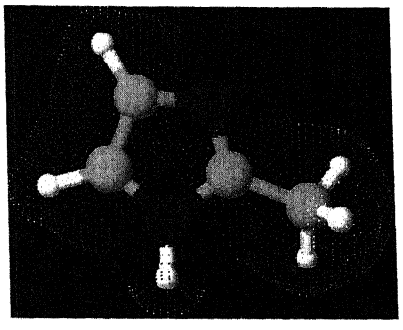



1-methyl-1H-imidazole






2-methyl-1*H*-imidazole



## *Table 4.1*

### *I.U.P.A.C. Name and Electron Configuration of the synthesized complexes*

| *S. No.* | *Compound* | *I.U.P.A.C. Name* | *Electron Configuration* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | Aquadicyanobis (imidazole)-nitrosylchromium (I) | $\{CrNO\}^5$ |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | Aquadicyanobis (1-methyl imidazole)-nitrosylchromium (I) | $\{CrNO\}^5$ |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | Aquadicyanobis (2-methyl imidazole)-nitrosylchromium (I) | $\{CrNO\}^5$ |

## *Table 4.2*

### *Analytical Data of the Complexes*

| *S. No.* | *Compound* | *% Cr Found (Calc.)* | *% C Found (Calc.)* | *% H Found (Calc.)* | *% N Found (Calc.)* |
|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | 16.54 (16.65) | 38.40 (38.47) | 3.21 (3.23) | 31.29 (31.40) |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | 16.37 (16.44) | 37.89 (37.98) | 4.41 (4.46) | 30.80 (31.01) |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | | | | |

## *Table 4.3*

### *Colour, Decomposition Temperature and % Yield of the Complexes*

| *S. No.* | *Compound* | *Colour* | *Decomposition Temperature (°C)* | *% Yield* |
|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | Brownish green | 260 | 55 |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | Greenish yellow | 265 | 45 |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | Yellowish brown | 268 | 50 |

## *Table 4.4*

### *Solubilities of the Complexes in different Solvents*

| S. No. | Compound | DMF | DMSO | EtOH | MeOH | Nitrobenzene | Ethylacetate |
|---|---|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | 60% | 65% | 35% | 20% | Insoluble | Insoluble |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | 55% | 60% | 30% | 15% | Insoluble | Insoluble |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | 50% | 45% | 25% | 15% | Insoluble | Insoluble |

## *Table 4.6*

### *Dehydration temperature and molecular weight of the Complexes*

| *S. No.* | *Compound* | *Dehydration temperature* | *molecular weight)* | |
|---|---|---|---|---|
| | | | *Found* | *Calculated* |
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | 115 | 311.21 | 312.23 |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | 112 | 315.02 | 316.26 |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | 112 | 315.02 | 316.26 |

## *Table 4.7*

## *Magnetic and ESR data of the Complexes*

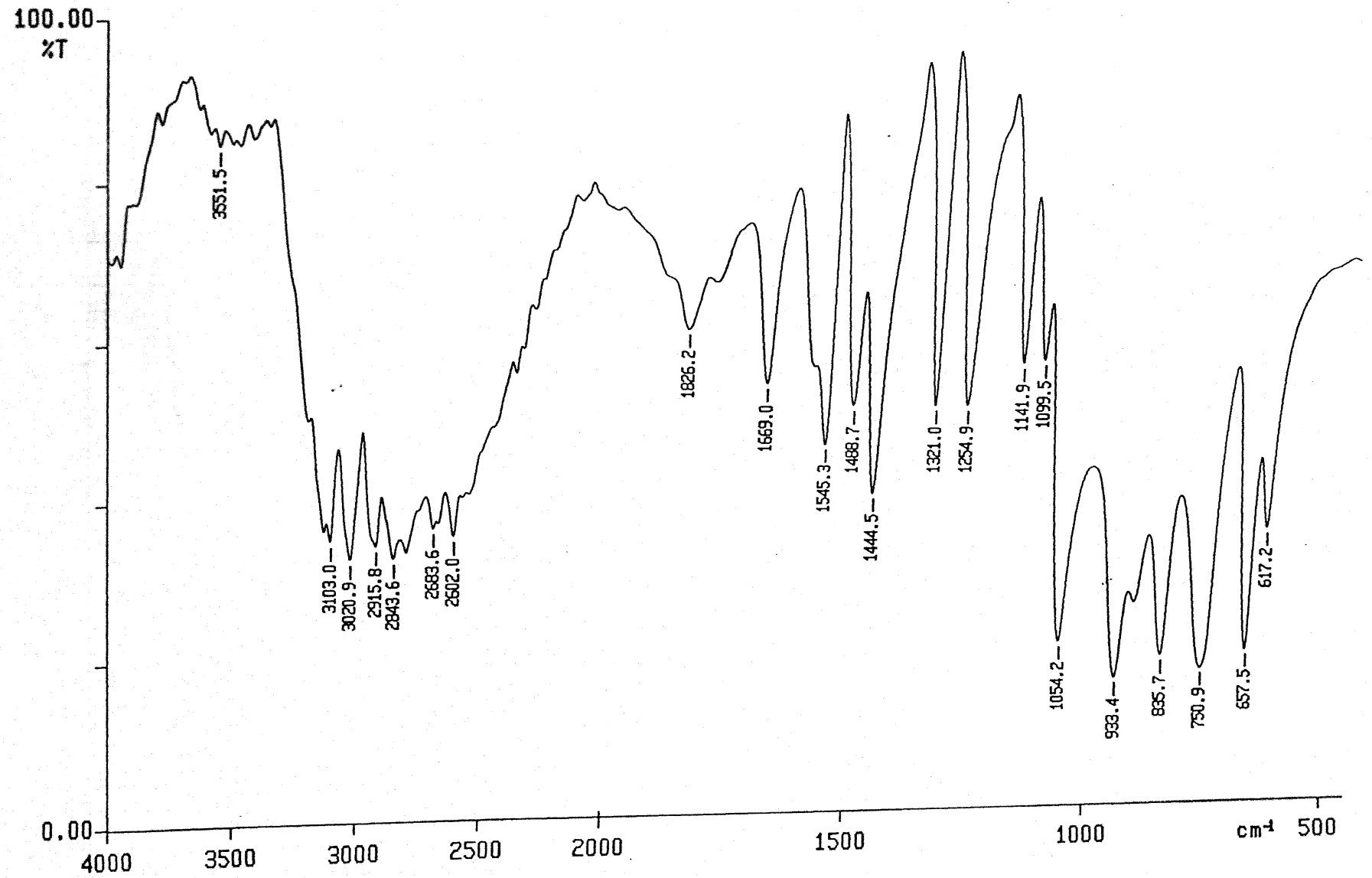
| *S. No.* | *Compound* | $\mu_{eff}$ | *'g'* |
|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | 1.72 | 1.984 |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | 1.74 | 1.985 |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | 1.74 | 1.985 |

## *Table 4.8*

### *Important IR spectral bands and their assignments*

| *S. No.* | *Compound* | $\nu_{(NO)}^{+}$ | $\nu_{(CN)}$ | $\nu_{(N\ cyclic)}$ | $\nu_{(OH)}$ |
|---|---|---|---|---|---|
| 1. | $[Cr(NO)(CN)_2(Imd)_2(H_2O)]$ | 1720 | 2150 | 1375 | 3580(br) |
| 2. | $[Cr(NO)(CN)_2(1\text{-M Imd})_2(H_2O)]$ | 1700 | 2160 | 1370 | 3575(br) |
| 3. | $[Cr(NO)(CN)_2(2\text{-M Imd})_2(H_2O)]$ | 1710 | 2155 | 1370 | 3580(br) |

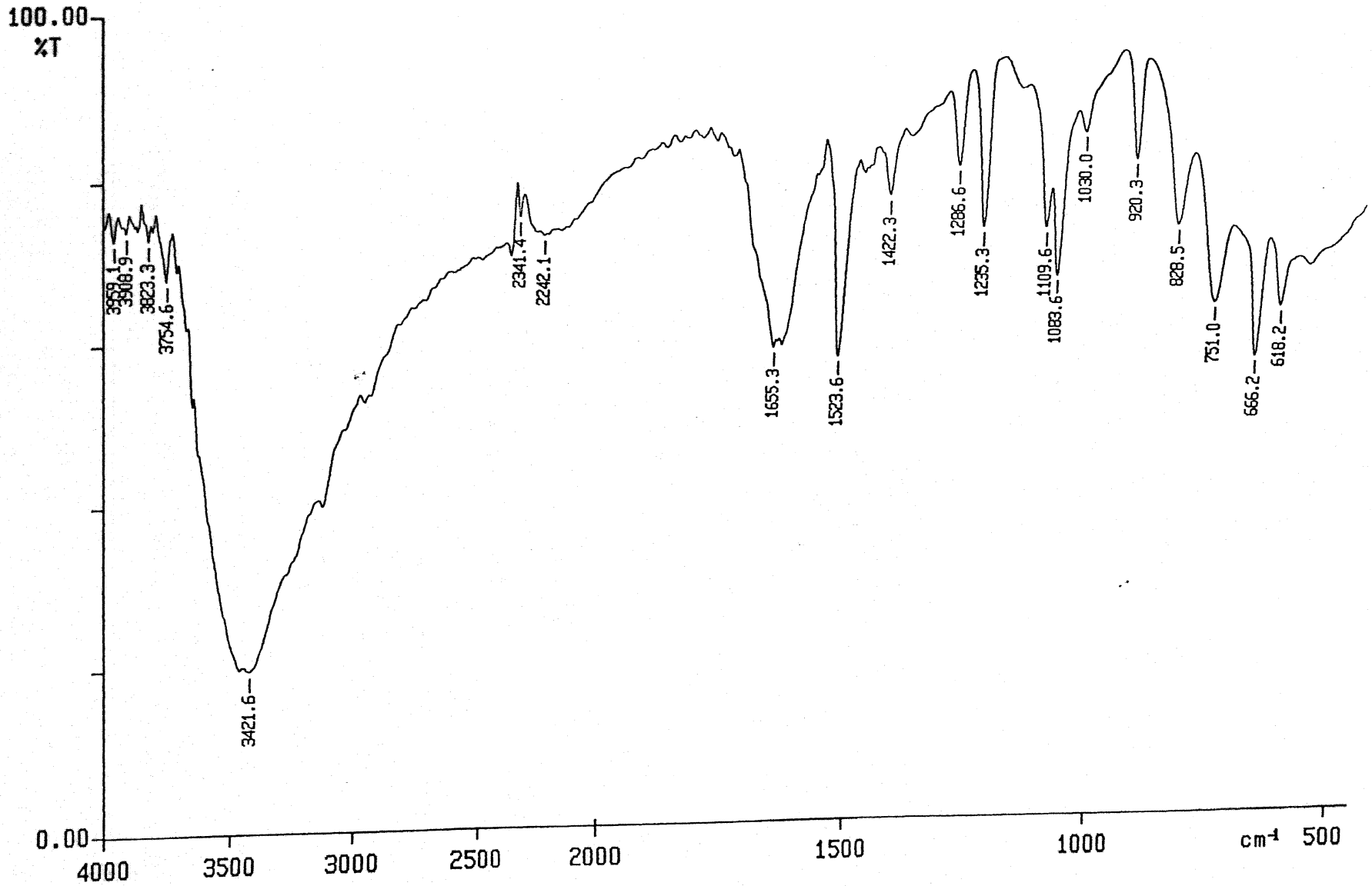
PERKIN ELMER




04/01/08 11:12 AH, CODE- M
X: 4 scans, 4.0cm-1, flat, smooth, abex
SAIF NO - 6809

**COORDINATION COMPOUND WITH IMIDAZOLE**

PERKIN ELMER

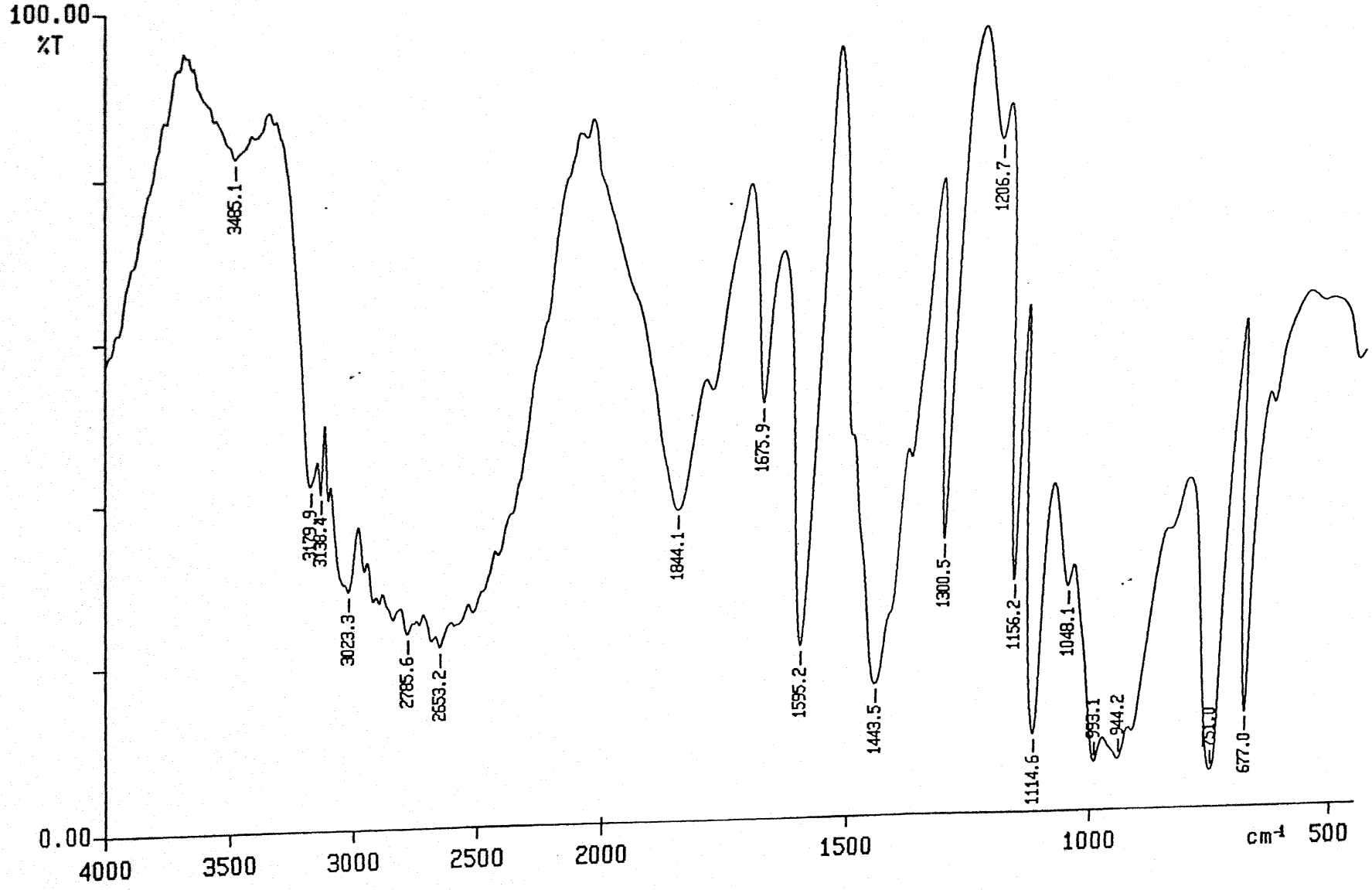



04/01/08 10:54 AH, CODE- E
X: 4 scans, 4.0cm-1, flat, smooth, abex

SAIF NO- 6809

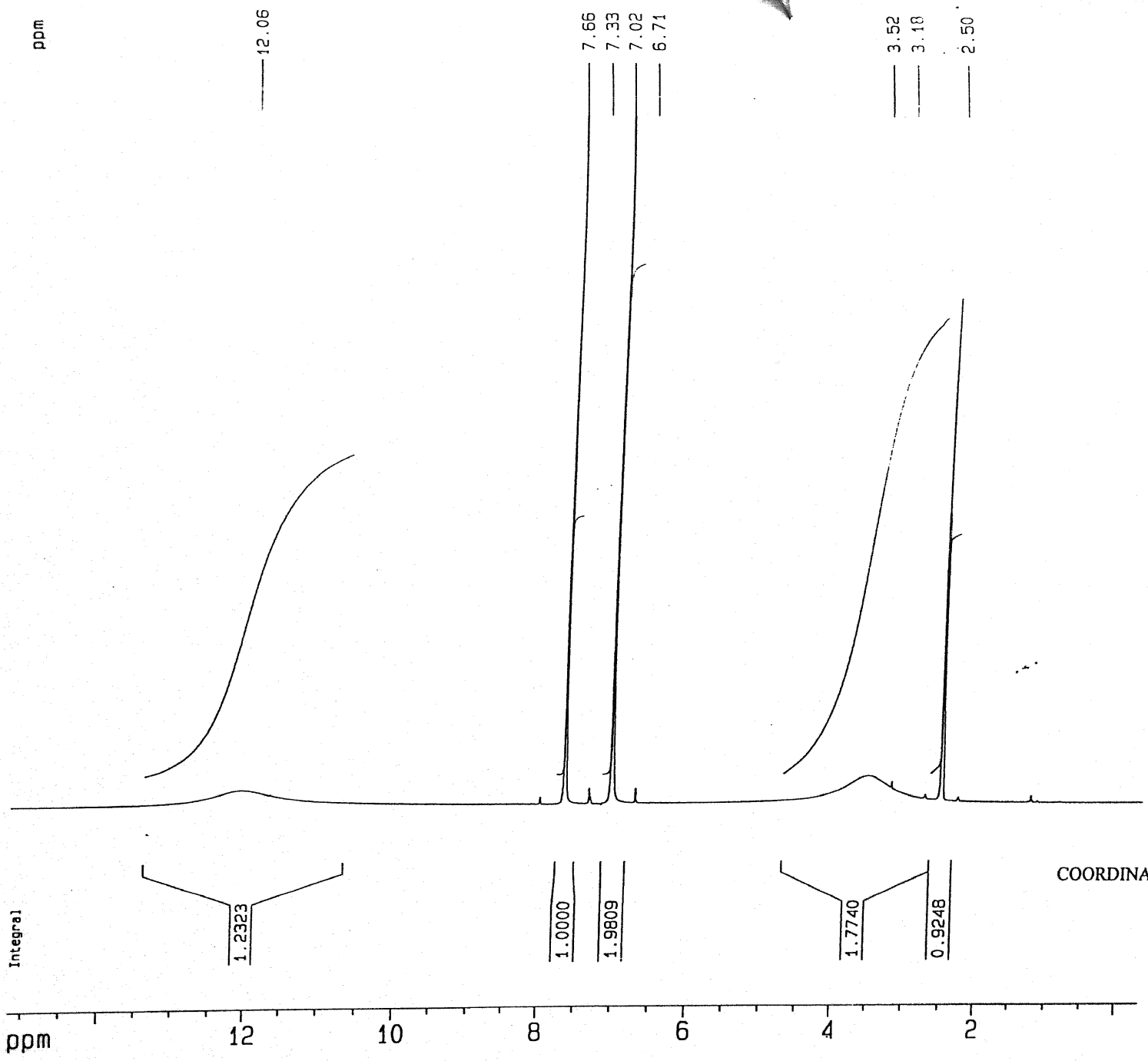
**COORDINATION COMPOUND WITH 1-METHYL IMIDAZOLE**

PERKIN ELMER




04/01/08 10:55 AH, CODE- F
X: 4 scans, 4.0cm-1, flat, smooth, abex
SAIF NO - 6809

**COORDINATION COMPOUND WITH 2-METHYL IMIDAZOLE**




Current Data Parameters
NAME [illegible]
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040303
Time 14.37
INSTRUM DRX300
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT DMSO
NS 20
DS 0
SWH 6580.555 Hz
FIDRES 0.254910 Hz
AQ 1.8574668 sec
RG 128
DW 57.600 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec

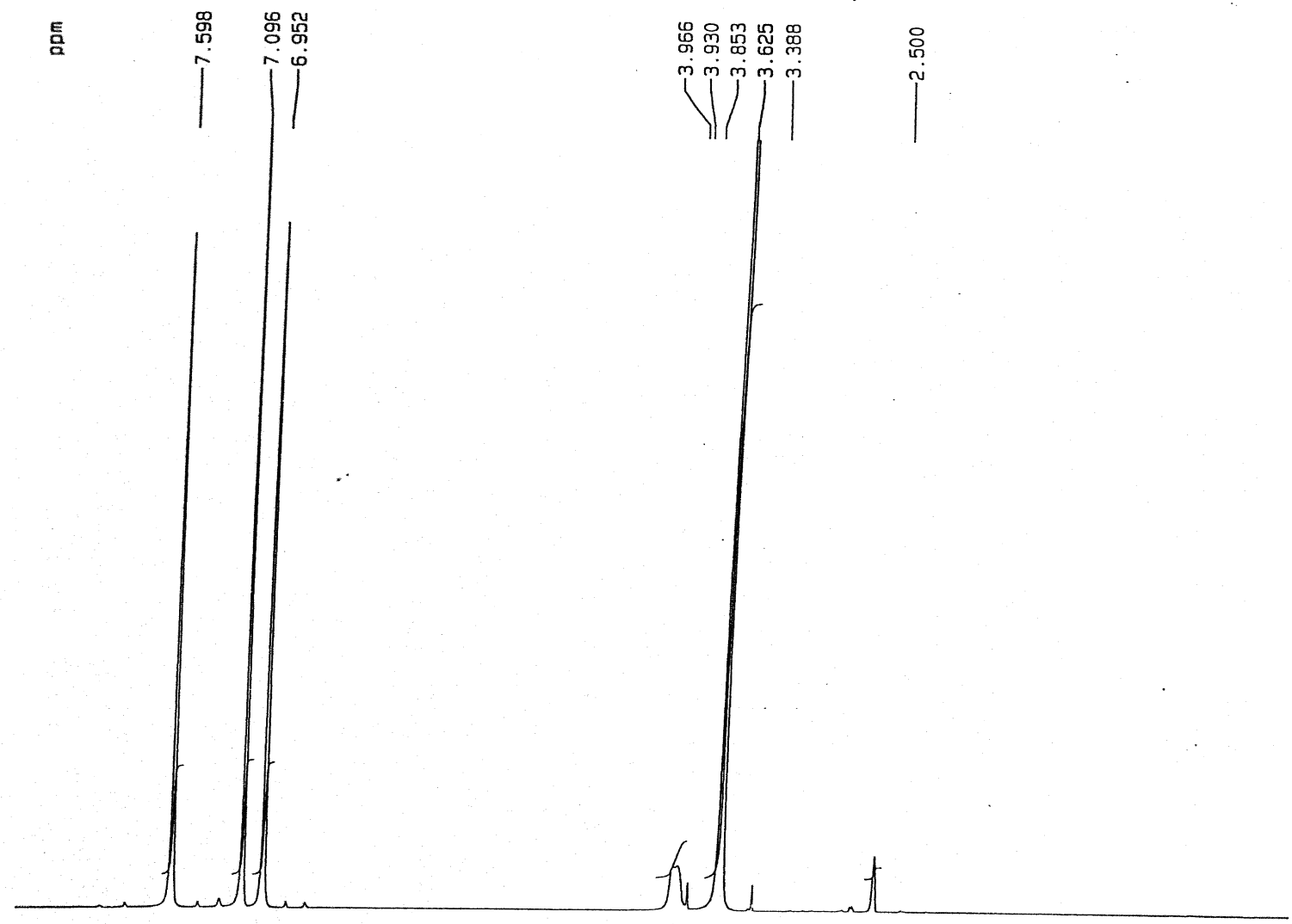
========== CHANNEL f1 ==========
NUC1 1H
P1 6.86 usec
PL1 -3.00 dB
SFO1 300.1321300 MHz

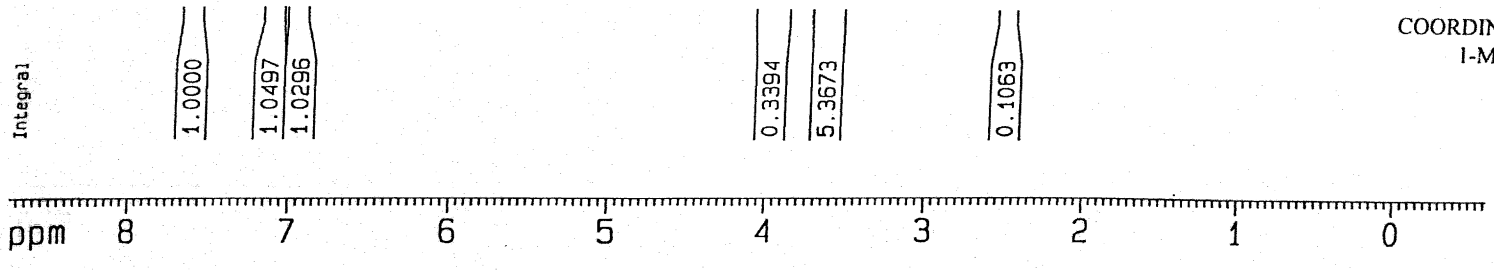
F2 - Processing parameters
SI 16384
SF 300.1300010 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.20

1D NMR plot parameters
CX 20.00 cm
F1P 15.167 ppm
F1 4552.14 Hz
F2P -0.345 ppm
F2 -103.69 Hz
PPMCM 0.77563 ppm/cm
HZCM 232.79131 Hz/cm

COORDINATION COMPOUND WITH IMIDAZOLE

M
RSIC NO.6809




Current Data Parameters

| | |
|---|---|
| NAME | 6809.e |
| EXPNO | 1 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20040303 |
| Time | 16.02 |
| INSTRUM | DRX300 |
| PROBHD | 5 mm Multinu |
| PULPROG | zg |
| TD | 32768 |
| SOLVENT | DMSO |
| NS | 32 |
| DS | 0 |
| SWH | 8680.556 Hz |
| FIDRES | 0.264910 Hz |
| AQ | 1.8874868 sec |
| RG | 16 |
| DW | 57.600 usec |
| DE | 6.00 usec |
| TE | 298.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 6.88 usec |
| PL1 | -3.00 dB |
| SFO1 | 300.1321300 MHz |

F2 - Processing parameters

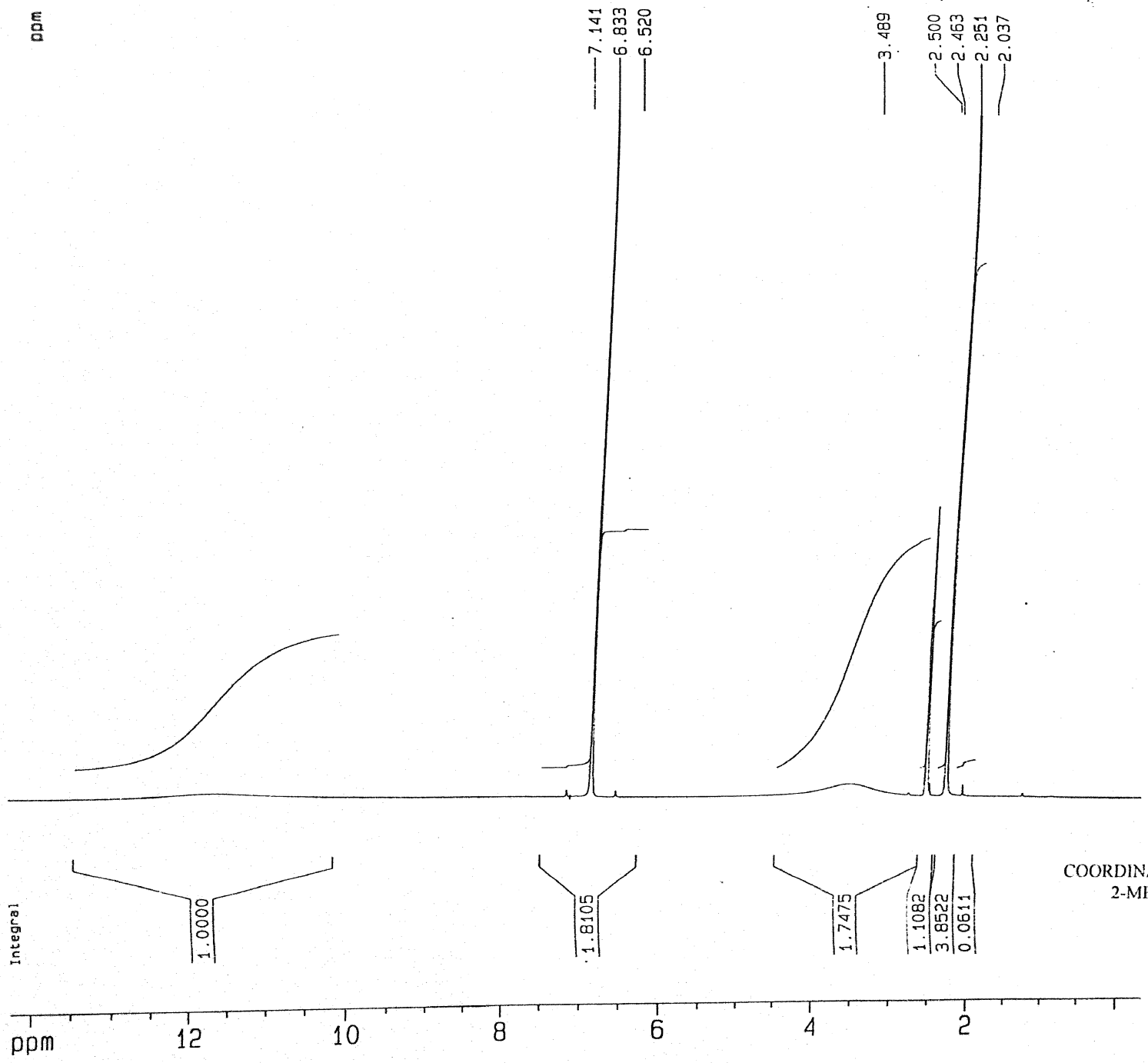
| | |
|---|---|
| SI | 16384 |
| SF | 300.1300010 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.10 Hz |
| GB | 0 |
| PC | 1.20 |

1D NMR plot parameters

| | |
|---|---|
| CX | 20.00 cm |
| F1P | 8.740 ppm |
| F1 | 2623.13 Hz |
| F2P | -0.623 ppm |
| F2 | -187.04 Hz |
| PPMCM | 0.46816 ppm/cm |
| HZCM | 140.50832 Hz/cm |

COORDINATION COMPOUND WITH
1-METHYL IMIDAZOLE

E




Current Data Parameters

| | |
|---|---|
| NAME | 6809 |
| EXPNO | 1 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20040303 |
| Time | 12.48 |
| INSTRUM | DRX300 |
| PROBHD | 5 mm Multinu |
| PULPROG | zg |
| TD | 32768 |
| SOLVENT | DMSO |
| NS | 32 |
| DS | 0 |
| SWH | 8680.556 Hz |
| FIDRES | 0.264910 Hz |
| AQ | 1.8874868 sec |
| RG | 57 |
| DW | 57.600 usec |
| DE | 6.00 usec |
| TE | 298.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 6.86 usec |
| PL1 | -3.00 dB |
| SFO1 | 300.1321300 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 16384 |
| SF | 300.1300010 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.10 Hz |
| GB | 0 |
| PC | 1.20 |

1D NMR plot parameters

| | |
|---|---|
| CX | 20.00 cm |
| F1P | 14.255 ppm |
| F1 | 4278.27 Hz |
| F2P | -0.345 ppm |
| F2 | -103.69 Hz |
| PPMCM | 0.73001 ppm/cm |
| HZCM | 219.09769 Hz/cm |

COORDINATION COMPOUND WITH
2-METHYL IMIDAZOLE

F
RSIC NO.6809

# Chapter V

## Biochemical Studies of synthesized coordination compounds of Chromium (I)

## Chapter V :

## Biochemical Studies of synthesized coordination compounds of Chromium (I)

Nitric oxide or nitrogen monoxide is a colorless gas formed by the combustion of nitrogen and oxygen as given by the reaction: energy $N_2 + O2 \rightarrow 2NO$; m.p. -163.6°C; b.p. -151.8°C. Nitric oxide readily combines with oxygen or air to form nitrogen dioxide ($NO_2$), which can again be separated by ultraviolet light to produce nitric oxide and highly reactive oxygen atoms. These oxygen atoms combine with hydrocarbons producing noxious compounds that irritate the membranes of living organisms and destroy vegetation. Large amounts of nitric oxide are created by internal-combustion engines and manufacturing processes. Its quantity is greatly reduced by passing the oxide gas through a catalyst, thereby converting it back to its constituent nitrogen and oxygen gases.

At room temperature and at atmospheric pressure nitric oxide is a colorless gas with low solubility in water (its electronic structure and other chemical and physical properties are shown in Fig. 1). Its hydrophobicity and, in consequence, its high diffusion rate in biological systems allows the molecule to reach the targets before

degradation. The diffusion distance of nitric oxide is in fact a matter of debate.

Although nitric oxide is a free radical it is relatively stable. It reacts predominantly with molecules that have orbitals with unpaired electrons, which are typically other free radicals ($O^{-}{}^{-}$ superoxide ion, $OH^{-}$) or transition metals like heme iron (hemoglobin, myoglobin, cytochromes,...). Reactions of nitric oxide differs between in vitro and in vivo systems. In vitro systems, the main degradation product of nitric oxide is $NO_2^-$ (nitrite), while in vivo the main product is $NO_3^-$ (nitrate) as a consequence of the reaction of nitric oxide with hemoglobin. In the environment, nitric oxide is a precursor of smog and acid rain. Nitric oxide in minute amounts serves as a source of energy in certain bacteria. In the body, it serves as a chemical messenger with a wide range of functions. It acts as a neurotransmitter and is necessary for penile erection. It affects blood pressure and is produced by macrophages in the immune system to help defend against infection and cancer. Despite its usefulness, nitric oxide can have a toxic effect on body cells and has been implicated in Huntington's disease and Alzheimer's disease. Nitric oxide (NO) is a soluble, highly reactive gas formed by natural chemical and physical reactions in the atmosphere. It is also produced by certain animal and plant cells from the amino acid, L-arginine. Because it is so small and diffusible NO passes through cell membranes and is often used as a biological signal.

In mammals NO helps to maintain blood pressure by dilating blood vessels, assists the immune system in killing invaders, and is a major factor in the control of penile erection. In the brain, NO

plays a role in development, neuron to neuron signaling, and probably contributes to the formation of memories.

Most non-pathological functions of NO are mediated by activation of an enzyme, guanylyl cyclase, or by nitrosylation of proteins. However, NO can also inhibit oxygen consumption by mitochondria and it is this action that is exploited in producing firefly light flashes.

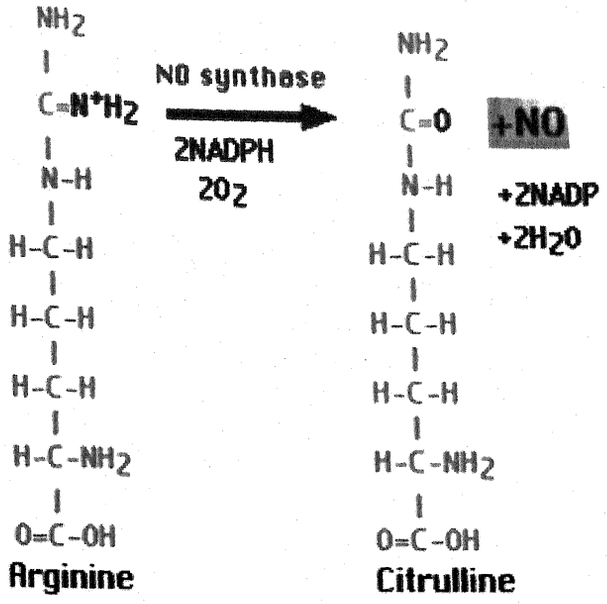
**Nitric Oxide Metabolism**

Nitric oxide (NO) is as a major signaling molecule in neurons and in the immune system, either acting within the cell in which it is produced or by penetrating cell membranes to affect adjacent cells. Nitric oxide is generated from arginine by the action of nitric oxide synthase (NO-synth). NO has a half-life of only a few seconds in vivo . However, since it is soluble in both aqueous and lipid media, it readily diffuses through the cytoplasm and plasma membranes. NO has effects on neuronal transmission as well as on synaptic plasticity in the central nervous system. In the vasculature, NO reacts with iron in the active site of the enzyme guanylyl cyclase (GC), stimulating it to produce the intracellular mediator cyclic GMP (cGMP), that in turn enhances the release of neurotransmitters resulting in smooth muscle relaxation and vasodilation. NO may also be involved in the regulation of protein activity through S-nitrosylation. In the extracellular milieu, NO reacts with oxygen and water to form nitrates and nitrites. NO toxicity is linked to its ability to combine with superoxide anions ($O^{-}$) to form peroxynitrite ($ONOO^{-}$), an oxidizing free radical that can cause DNA fragmentation and lipid oxidation. In the

mitochondria, $ONOO^-$ acts on the respiratory chain (I-IV) complex and manganese superoxide dismutase (MnSOD), to generate superoxide anions and hydrogen peroxide ($H_2O_2$), respectively.

But NO also has many physiological functions.

They share these features:




NO is synthesized within cells by an enzyme **NO synthase (NO-synth)**.

The human (and mouse) genome contains 3 different genes encoding NO synthases.

- **n NO-synth** (or NO-synth-1):found in neurons (hence the "n").
- **i NO-synth** (or NO-synth-2): found in macrophages. (the "i" stands for "inducible". Whereas the levels of nNO-synth and eNO-synth are relatively steady, expression of iNO-synth genes awaits an appropriate stimulus (e.g., ingestion of a parasite).

- **eNO-synth** (or NO-synth-3): found in the endothelial (hence the "e") cells that line the lumen of blood vessels.

- All types of NO-synth produce NO from arginine with the aid of molecular oxygen and NADPH.
- NO diffuses freely across cell membranes.
- There are so many other molecules with which it can interact, that it is quickly consumed close to where it is synthesized.
- Thus NO acts in a paracrine or even autocrine fashion — affecting only cells near its point of synthesis.

Some of the functions of NO are discussed below

**Blood Flow**

NO relaxes the smooth muscle in the walls of the arterioles. At each systole, the endothelial cells that line the blood vessels release a puff of NO. This diffuses into the underlying smooth muscle cells causing them to relax and thus permit the surge of blood to pass through easily. Mice whose genes for the NO synthase found in endothelial cells (eNO-synth) has been "knocked out" suffer from hypertension.

Nitroglycerine, which is often prescribed to reduce the pain of angina, does so by generating nitric oxide, which relaxes the walls of the coronary arteries and arterioles.

Three of the pioneers in working out the biological roles of NO shared a Nobel Prize in 1998 for their discoveries. The award to one of them, Ferid Murad, honored his discovery that nitroglycerine works by releasing NO. This seems particularly appropriate because Alfred Nobel's fortune came from his invention of making dynamite from nitroglycerine!

NO also inhibits the aggregation of platelets and thus keeps inappropriate clotting from interfering with blood flow.

**Skin**

Evidence of nitric oxide (NO) synthesis by human skin cells was first reported near 12 years back. It is well stablshed fact that NO plays a key role in orchestrating the skin's response to external stimuli such as heart, ultraviolet light, response to infection and wound healing under certain pathological conditions.

The NO liberated following UV irradiation plays a significant role in initiating melanogenesis, erythema, and immunosuppression. New evidence suggests that it may also be involved in protecting the keratinocytes against UV-induced apoptosis.

The enhanced NO-synth activity in skin wounding appears to be important in guiding the infiltrating white blood cells and initiating the inflammation. In response to both results, UV irradiation and skin wounding, the activation of constitutive NO-synth proceeds and overlaps with the expression of NO-synth-2. Thus, at a macro-level, at least three different rates of NO production can occur in the skin, which seem to play an important part in organizing the skin's unique adaptability and function.

## Kidney Function

Release of NO around the glomeruli of the kidneys increases blood flow through them thus increasing the rate of filtration and urine formation.

## Binding of NO to Synthetic Heme-Thiolate complex

Nitric oxide (NO) fulfills important roles in mammalian biology as an intracellular signaling agent for a variety of biological functions, such as vasodilation, neurotransmission, bronchodilation, and cytotoxic immune response. Much of the biochemistry of this molecule involves heme proteins, including the biosynthesis of nitric oxide and signal transduction mediate by NO. In this context, recent studies have been concerned with the preparation and mechanistic evaluation of synthetic iron(III/II)porphyrin complexes as useful biometric model systems in simulating the mechanism of heme ligand binding and activation and thereby, determining the distinctive features of the active site of heme proteins. Of significant interest is the high reactivity of model porphyrins coupled to the ability to undergo fast ligand substitution and redox cycling. While the NO binding to heme-imidazole complexes has been the subject of many investigation, fewer studies have been carried out with synthetic NO-Heme-Thiolate adducts, in part because the thiolate –coordinated heme models tend to be unstable under the employed experimental conditions. Most of the synthesized thiolate-ligated iron porphyrins in the absence of bulky protecting groups around the axial sulfur atom were found to be very sensitive to light and air.

Higuchi and co-workers first prepared a stable $Fe^{III}$-porphyrin alkanethiolate complex, in which the thiolate ligand is sterically protected by bulky pivaloyl groups. The $SR(Fe^{III})$ complex is known to have similar reactivity to that of cytochrome P450. Furthermore, due to the introduction of bulky groups on the R-S coordination face of the porphyrin molecule, the thiolate complex is unique in that it retains its axial thiolate to be stable during catalytic oxidations. It was also established that the thiolate ligand plays an important role in the characteristic oxidizing ability of the $SR(Fe^{III})$ complex, which has a marked influence on the reactivity of the high valent iron-oxo porphyrin intermediate.

Recently, the first synthetic $SR(Fe^{III}NO)$ complex was prepared and characterized with the application of spectroscopic (UV-VIS, EPR and IR) and electrochemical (cyclic voltammetry) methods. The studies revealed that NO coordinates reversibly to the $Fe^{III}$ centre of SR in benzene solution, and the thiolate ligand does not undergo modification during this process (e.g., formation of a nitrosothiol). The resulting SR-NO complex exhibits ν(N-O) and ν(Fe-N) modes very close to those of neutral heme-thiolate containing enzymes and differs from those of heme-imidazole containing enzymes. The nitric oxide complex of $SR(Fe^{III})$ appeared to be diamagnetic (EPR-silent), whereas the parent SR complex showed a typical low spin signal of an $Fe^{III}$-porphyrin-thiolate complex.

Since the $SR(Fe^{III})$ complex reversibly binds nitric oxide, the NO-heme-thiolate adduct can be considered as a useful and valuable model for nitric oxide synthase (NO-synth) and nitric oxide reductase ($P450_{nor}$). Cytochrome $P450_{nor}$ is an enzyme that

catalyses the reduction of NO to $N_2O$, with electrons directly transferred from NADH ($2NO + NADH + H^+ \rightarrow N_2O + H_2O + NAD^+$). On the basis of spectroscopic and kinetic data, Shiro et al. proposed that the overall enzymatic reaction involving consists $P450_{nor}$ of three chemical reactions, according to scheme 1

$$Fe^{3+} + NO \longrightarrow Fe^{3+}NO$$

$$Fe^{3+} + NO + NADH \longrightarrow I^+ + NAD^+$$

$$I^+ + NO + H^+ \longrightarrow Fe^{3+} + N_2O + H_2O$$

The first intermediate in this catalytic cycle is the stable ferric-NO complex, $P450_{nor}(Fe^{III}\text{-}NO)$. Reduction of the later by NADH yields an intermediate (Fe-NO)complex (I) with an absorption maximum at 444nm, whose identity is still controversial. The formation of I is the rate determining step of the overall reaction. The reactions of wild type and mutant forms of the $P450_{nor}$ enzyme with NO and NADH have been the subject of many spectroscopic (EPR, UV-VIS, resonance Raman, infrared, and X-ray absorption), kinetic (stopped flow rapid scan and flash photolysis), and computational (DFT and semiempirical) studies. The crystal structure of the $P450_{nor}(Fe^{III}\text{-}NO)$ showed a slightly tilted and bent NO binding of the $Fe^{III}$ atom, in contrast to the highly bent coordination found for the nitrosyl complexes ferrous hemoproteins. Such a NO coordination geometry can be explained in terms of electronic (*trans* effect from the *Cis* thiolate ligand) and steric effects around the $Fe^{III}$-NO moiety.

### *Other Actions on Smooth Muscle*

**Peristalsis**

The wavelike motions of the gastrointestinal tract are aided by the relaxing effect of NO on the smooth muscle in its walls.

**Birth**

NO also inhibits the contractility of the smooth muscle wall of the uterus. As the moment of birth approaches, the production of NO decreases.

Nitroglycerine has helped some women who were at risk of giving birth prematurely to carry their baby to full term.

### *NO and Inflammation*

The NO produced by NOS-3 inhibits inflammation in blood vessels. It does this by blocking the exocytosis of mediators of inflammation from the endothelial cells.

NO may also block exocytosis in other types of cells such as macrophages and cytotoxic T lymphocytes (CTL).

### *Effects on Secretion*

NO affects secretion from several endocrine glands.

For examples, it stimulates

- the release of Gonadotropin-releasing hormone (GnRH) from the hypothalamus;
- the release of pancreatic amylase from the exocrine portion of the pancreas;

- The release of adrenaline from the adrenal medulla.

***NO and fertilization***

The acrosome at the tip of sperm heads activates its NO synthase when it enters the egg. The resulting release of NO in the egg is essential (at least in sea urchins) for triggering the next steps in the process:

- blocking the entry of additional sperm and
- Orienting the pronuclei for fusion.

***Killing Pathogens***

NO aids in the killing of engulfed pathogens (e.g., bacteria) within the lysosomes of macrophages.

Mice whose genes for the NO synthase found in macrophages (iNOS) have been knocked out are more susceptible to infections by intracellular bacteria like Listeria monocytogenes.

Th1 cells, the ones responsible for an inflammatory response against invaders, secrete NO.

Harmless bacteria, living as commensals at the rear of our throat, convert nitrates in our food into nitrites. When these reach the stomach, the acidic gastric juice (pH ~1.4) generates NO from them. This NO kills almost all the bacteria that have been swallowed in our food.

(Since the dawn of recorded human history, nitrites have been used to preserve meat from bacterial spoilage.)

***Biochemistry of NO in skin***

In simple terms, NO is synthesized by the intracellular enzyme. NO synthase (NO-synth), in a two- step oxidation of L-anginine, that produces of equal parts of citrulline and NO**(7-9)**. Although in the literature, it is almost taken for granted that NO-synth produces the free radical, NO, this is still under debate, since other nitrogen oxide species could result from this catalytic process see **(10)**.

The three main NO-synth isoforms currently identified are, NO-synth-1, originally isolated from neuronal tissue (also known as nNO-synth), NO-synth-2 (or iNO-synth), an inducible isoform, and NO-synth-3 (or eNO-synth), predominant in the endothelium **(10-20)**. (An isoform named mtNO-synth has also recently been isolated in mitochondria **(13)**. They all exist as homodimers, with molecular weights between 130 and 160 kDa, and all require the cofactors, flavin dinucleotide, flavin mononucleotide, tetrahydrobiopterin, and reduced nicotinamide adenine dinucleotide phosphate. They also require bound calmodulin, but whereas NO-synth-1 and NO-synth-3 require $Ca^{2+}$ -calmodulin, the NO-synth-2 appears to have lost this calcium dependence. In addition to requiring these cofactors, the activity of the NO-synth isozymes is regulated by associated proteins and by their localization inside cells **(14, 15)**. For example, NO-synth-3 in endothelial cells is regulated in part by its distribution between the caveolae (specialized plasma membrane structures) and intracellular pools, in a process that involves palmitoylation and the recently characterzed proteins, nosip and nostrin **(16, 17)**. Further more, its activity is also controlled by dynamic associations with regulatory proteins in the caveolae including caveolin- 1,

hsp90, and transmitter receptors, as well as by phosphorelation **(18, 19)**.

NO-synth-1 and NO-synth-2 are active as cytoplasmic enzymes and yet could also function to be membrane associated proteins **(15)**. NO-synth-1 possesses a PDZ-binding motif with which it can interact with a number of other proteins. In particular, via the PDZ motif, NO-synth-1 is reported to make stimulatory association with the $5HT_{2b}$ receptor and an inhibitory association with the calcium ATPase **(10, 20, 21)**.

The role of endogenous NO-synth inhibiters in basic skin physiology is still to be established. The arginine metabolite, asymmetric dimethylarginine (ADMA), has been shown to be an important competitive NO-synth inhibitor in cardiovascular physiology **(22)** and it may also play a role in the skin. Another point of regulation is the supply of the substrate, arginine by other cellular pathways and the presence of endogenous NO-synth inhibitors have been invoked to explain the "arginine parabox": situations where L-arginine supplementation stimulates NO synthesis, despite apparently saturating extracellular arginine concentrations **(23, 24)**.

NO is highly diffusible and highly reactive. Instead of activating downstream pathways via traditional receptor-mediated events, it modulates the activity of a number of divers molecules. Wink and Mitchell **(25)** classified these NO reactions as being either direct (on the biological mediator) or indirect (involving reactive nitrogen and oxygen species). The direct downstream pathways consist mainly of interaction between NO and heme-containing proteins, the most important being guanylate cyclase **(11,26)**. Activation of this enzyme, by NO, induces the production

guanosine cyclic 3'-5'- monophosphate (cGMP) which in turn activates protein kinase G (PKG). this downstream pathway is particularly important in mediating the effects of the low levels of NO production, which seem to occur with constitutive NO-synth activation. The indirect downstream pathways, which become more important under high local concentrations of NO, involve the formation of nitrogen oxide species such as $N_2O_3$, HNO (nitroxyl), and ONOO-(peroxinitrite) **(27)**. These molecules, in turn, modify thiol-containing proteins, either by nitrosation ($N_2O_3$) or oxidation (HNO and ONOO-). The selection of which indirect downstream pathway is chosen seems to depend, to some extent , on the redox potential of the cell **(28-30)**. The existence of biological NO donors in the cytoplasm has been suggested for some time **(31,32)** but, the identify and function of these remain unclear. Some of the early work of Fuchgott and colleagues showed that 'stored' NO in vascular tissue could be modilized by UV irradiation to induce NO-dependent smooth muscle relaxation (see **33**). In the lung, putative endogenous NO donor can induce the S-nitrosylation of 5-HT2 receptors **(34)**. The evidence points to such stores as being perhaps S-nitrosoglutathione (GSNO) or a "GSNO-like compound," although other nitrogen compounds may also be involved **(33-35)**. The existence of a putative NO store in the skin has previously been suggested **(36, 37)**, but its identity has not been elucidated. Since GSNO is readily formed from $N_2O_3$ and glutathione **(9)**, it seems likely that GSNO may also represent an No 'store' in skin cells that express NO-synth.

**Interaction of nitric oxide with mitochondria: regulation and impact on pathology**

The most sensitive of the signaling pathways are those involving in nitrosylation of metalloproteins at ferrous heme centres. The two examples for which this mode of action has been defined are soluble guanylate cyclase and the newly discovered NO-cytochrome c oxidase signaling pathways is evident with activation of sGC having recently been linked to control of mitochondrial biogenesis. Higher concentrations of NO appear to selectively depress the activity specific mitochondrial proteins and render endothelial cells more susceptible to apoptosis. The function of the interaction of NO with mitochondria is oxygen sensitive and shows the greatest inhibition for mitochondria that are actively respiring. Under various pathological conditions the NO-dependant regulation is subject to modification in response to hypoxic stress. The mechanism and control of the NO-mitochondrial pathway will be described and the interactions under conditions of oxidative stress dicussesed.

# BIBLIOGRAPHY


1. C. M. Lukehart and J. N. Troup, Inorg. Chim. Acta., 22, 81, 1977.
2. S. Sarkar, R. C. Maurya and S. C. Chaurasia, Indian J. of Chem., 14A, 285, 1976.
3. R. C. Maurya and R. K. Shukla, Indian J. of Chem., 59, 340, 1982.
4. R. C. Maurya, Indian J. of Chem., 22A, 529, 1983.
5. R. C. Maurya, R. K. Shukla, M. R. Maurya, and N. Anandam, J.Indian Chem. Soc., 62,63 (1985).
6. R. C. Maurya, R. Shukla, R. K. Shukla, N. Anandam, M. R. Maurya and W. U. Malik, Proc. Physical Sciences, 52A, 1428 (1986).
7. R. C. Maurya, R. Shukla, N. Anadam, S. K. Srivastava and W. U. Malik, Transition Met. Chem., 12, 203 (1987).
8. R. C. Maurya, R. Shukla, D. C. Gupta, R. K. Shukla, N. Anandam, and W. U. Malik, Synth. React. Inorg. Met-org.Chem. 16 (9), 1243,(1986).
9. W. P. Griffith and G. Wilkinson, J. Chem. Soc., 872, 1959.
10. R. C. Maurya, R. Shukla, R. K. Shukla, N. Anandam, D. C. Gupta, and M. R. Maurya, Synth. React. Inorg. Met-Org.Chem. 16 (8), 1059,(1986).
11. R. C. Maurya, R. Shukla, R. K. Shukla and N. Anandam, Proc. XXIV-1C-CC,A-6, 402, Athens, Greece (1986).
12. R. C. Maurya and D. D. Mishra, Synth. React. Inorg. Met-Org.Chem. 18, 133, (1988).

13. R. C. Maurya and D.D. Mishra, Transition Met. Org.Chem. 12, 551, (1987).

14. R. C. Maurya and D. D. Mishra, Synth. React. Inorg. Met-Org.Chem. (In Press).

15. J. H. Enemark and R. D. Feltham, Coord. Chem. Rev. 13, 339 (1974).

16. Wiliiams et al., J. Am. Chem. Soc., 57, 229, 536 (1935); 58, 1063, (1936).

17. Fosbinder and Walter, J. Am. Chem. Soc., 61, 2032, (1939).

18. Clarke et al., Science, 102, 627, (1945); The Chemistry of Penicillin, Princeton University Press, (1949).

19. Erlenmayer, Bauman and Sorkin, Helv.Chem.Acta., 31, 1978 (1948).

20. Erlenmayer er al., Helv.Chem.Acta., 23, 1268 (1940).

21. Erlenmayer er al., Helv.Chem.Acta., 20, 204 (1937); 25, 515 (1942); 29, 1946 (1946).

22. Bamberger, Ber., 24, 1758, (1891).

23. Erlenmayer er al., (a) Helv.Chem.Acta., 15, 1171 (1932); (b) 16, 733 (1933); (c) 16, 897 (1933); (d) 16, 1381 (1933); (e) 20, 310, 514 (1937); (f) 21, 709, 1665, 111, 1010 (1938); (g) 22, 851 (1939); (h) 25, 515 (1942).

24. Bradlow, Vanderwerf and Kleinberg, J. Chem. Edu., 24, 433, (1947).

25. Erlenmayer and Ueberwasser, Helv.Chem.Acta., 23, 1268 (1940).

26. Carmack er al., J. Am. Chem. Soc., 71, 84, 231, 288 (1949).

27. Phillips, Hunter, and Sutton, J. Chem. Soc., 1945, 146; cf. Sutton, Ann. Repts. Progr. Chem. (Chem. Soc. London), 37, 74–75 (1940).

28. Schomaker and Pauling, J. Am. Chem. Soc., 61, 1769 (1939).

29. F. Bernardi, L. Forlani, P. E. Todesco, F. P. Colonna and G. Distefano, J. Electron. Spectrosc., 9, 217 (1976).

30. M. Gelus, P. M. Vay, and G. Berther, Theor. Chem.acta., 9, 182, (1967).

31. I. N. Bojesen, J. H. Hoeg, J. T. Nielsen, I. B. Petersen and K. Schaumburg, Acta Chem. Scand., 25, 2739, (1971)

32. G. Saloma, Y. Ferre and E. J. Vincent, J.Chim. Phys. 69, 1292 (1972).

33. L. Nygaard, E. Asmussen, J. H. Hoeg, R. C. Maheswari, C. H. Nielsen, I. B. Petersen, J. Rastrup-Anderson, and C. O. Sorensen, J. Mol. Sructure, 8, 225 (1971).

34. B. Bak, D. Cristensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, J. Mol. Spectrosc, 7, 58 (1961).

35. G. Leandri, A. Mangini, F. Montanavi, and P. Passerini, Gazz. Chim. etal. Raynor & co-workers 85, 769 (1955).

36. Y. N. Sheinker, V. V. Kushkin, and I. Y. Postovskii, Zh. Fiz. Khim, 31, 214 (1957).

37. N. Colebourne, R. G. Foster, and E. Robson, J. Chem. Soc. C, 685 (1967).

38. G. Sbrana, E. Castellucci, and M. Ginanneschi, Spectrochim.Acta, A23, 751 (1967).

39. G. Davidovics, C. Garrigou Lagrange, J. Chouteau, and J. Metzger, Spectrochim.Acta, A23, 1477 (1967).

40. B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, J. Mol. Spectrosc, 2, 361 (1958).

41. A. Taurins and W. G. Schneider, Can. J. Chem. 38, 1237 (1960).

42. B. Bak, J. T. Nielsen, J. Rastrup-Anderson and M. Schottlaender, Spectrochim.Acta, 18, 741 (1962).

43. P. C. Haake and W. B. Miller, J. Am. Chem. Soc., 85, 4044 (1963).

44. H. A. Staab and A. Mannschreck, Chem. Ber., 98, 1111 (1965).

45. T. Schaefer and W. G. Schneider, J. Chem. Phys., 32, 1224 (1960).

46. G. Borgen and S. Gronowitz, Acta Chem. Scand.., 20, 2593 (1966).

47. E. J. Vincent, R. Phan Tan Luu, J. Metzger, and J. M. Surzur, Bull. Soc. Chim. France, 11, 3524 (1966).

48. J. P. Aune, R. Phan Tan Luu, E. J. Vincent, and J. Metzger, Bull. Soc. Chim. France, 7, 2679 (1972).

49. R. Phan Tan Luu, L. Bouscasse, E. J. Vincent, and J. Metzger, Bull. Soc. Chim. France, 9, 3283 (1967).

50. E. J. Vincent, R. Phan Tan Luu, and J. Metzger, Bull. Soc. Chim. France, 11, 3537 (1966).

51. R. J. Abraham and W. A. Thomas, J. Chem. Soc. B, 127 (1966).

52. J. Devanneaux and J. F. Labarre, J. Chim. Phys. Physicochim. Biol., 66, 1780 (1969).

53. G. Davidovics, Thesis, University of Marseille, France (1969).

54. M. A. Soulie, P. Goursot, A. Peneloux, and J. Metzger, J. Chim. Phys., 66, 603 (1969).
55. M. A. Soulie, D. Bares, and J. Metzger, C. R. Acad. Sci. Ser. C., 281, 341 (1975).
56. M. A. Soulie, P. Goursot, A. Peneloux, and J. Metzger, C. R. Acad. Sci. Ser. C., 267, 114 (1968).
57. R. Mayer, G. Bourrelly and J. Metzger, Bull. Soc. Chim. France, 5, 1711 (1967).
58. R. Mayer and J. Metzger, Bull. Soc. Chim. France, 5, 1711 (1967).
59. R. Arnaud, M. Gelus, J.C. Mallet, and J. M. Bonnier, Bull. Soc. Chim. France, 9, 2857 (1966).
60. P. Goursot, and I. Wadso, Acta Chem. Scand., 20, 1314, (1966).
61. A. Albert and R. Goldacre, J. Chem. Soc., 2240 (1948).
62. D. Haake and L. P. Bauscher, J. Phys. Chem., 20, 145 (1952).
63. L. Arapides, Justus Liebigs Ann. Chem., 249, 7, (1888).
64. A. Hantzsch, Justus Liebigs Ann. Chem., 250, 257, (1889).
65. H. Erlenmayer and E. H. Schmid, Helv.Chem.Acta., 22, 698 (1939).
66. H. Erlenmayer and E. H. Schmid, Helv.Chem.Acta., 24, 869 (1941).
67. W. J. Eilbeck, F. Holmes, and A. E. Underhill, J. Chem. Soc. A, 757 (1967).
68. J. A. Weaver, P. T. Hambright, P. T. Albert, E. Kang, and A. Thorpe, Inorg. Chem., 9, 268 (1970).

69. M. N. Hughes and K. J. Rutt, Inorg. Chem., 10, 414 (1971).

70. M. N. Hughes and K. J. Rutt, J. Chem. Soc. A, 18, 3015 (1970).

71. A. W. Addison, K. Dawson, R. D. Gillard, B. T. Heaton, and H. Shaw, J. Chem. Soc. Dalton Trans., 5, 589 (1972).

72. K. H. Pannell, C. C. Y. Lee, C. Parkanyi, and R. Redfearn, Inorg. Chim. Acta, 12, 127 (1975).

73. A. Earnshaw "Introduction to Magnetochemistry" Academic press, New York.

74. Figgis and Lewis, "Modern Coordination Chemistry" Edited by Lewis and Wilkins, Interscience (1960).

75. P. Griess, Chem. Ber., 12, 427 (1963)

76. J. Burgees, B. A. Goodman and J. B. Raynor, J. Chem. Soc. (A), 501, (1968).

77. H. Gamsjager and R. K. Murmann, Adv. Inorg. Bioinorg. Mech., 2, 317 (1982).

78. D. R. Stanks and T. W. Swaddle, J. Am. Chem. Soc., 93, 2783 (1971).

79. N. V. Duffy and J. E. Swaddle, J. Am. Chem. Soc., 89, 272 (1967).

80. T. W. Swaddle and D. R. Stanks, J. Am. Chem. Soc., 94, 8357 (1972).

81. I. S. Ahuja and P. Rastogi, J.Inorg. Nucl. Chem., 32, 2085, (1970).

82. I. S. Ahuja and P. Rastogi, J. Chem. Soc., 1894, (1969).

83. D. S. Jamgekar, S. D. Angadi and V. H. Kulkarni, Natl. Acad. Sci. Lett., 20, 133 (1997).

84. I. S. Ahuja and C. L. Yadav, Indian J. of Chem., 27A, 166, (1963).

85. P. T. Manoharan and H. B. Grey, Inorg. Chem., 5, 823, (1966).

86. L. S. Meriwether, S. D. Robinson, and G. Willkinson, J. Chem. Soc., 1488 (1966).

87. K. Nakamoto "Infrared and Raman spectra of Inorg. and coordination compounds" 3rd Edition, John Wiley and Son's New York (1978).

88. A. D. Cross, "An Introduction to practical Infrared spectroscopy" Butterworth Scintific publications, London, P-65, (1960).

89. B.S. Manhas and V. K. Bhatia, Indian J. Chem., 10, 947 (1972)

90. B.S. Manhas, V. K. Bhatia and O. P. Chitkara, Indian J. Chem. A, 10, 206 (1976).

91. E. J. Duff, M. N. Hughes and K. J. Rutt, Inorg. Chem. Acta, 6, 408 (1972).

92. P. P. Singh and A. K. Srivastava, J. Inorg. Nucl. Chem., 36, 928 (1974).

93. P. P. Singh and A. K. Srivastava, Austr. J. Chem., 27, 509 (1974).

94. P. P. Singh and U. P. Shukla, Austr. J. Chem., 27, 1827 (1974).

95. R. Phan Tan Luu, J. M. Surzur, J. Metzger, J. P. Aune, and C. Dupuy, Bull. Soc. Chim. France, 9, 3274 (1967).

96. A. Danek, J. Kwiek and W. Sztark, Diss. Pharm. Pharmacol., 18, 423 (1966).

97. H. Najer, J. Armand, J. Menin and N. Voronine, Compt. Rend., 260, 4343 (1965).

98. L. Bouscasse, Unpublished Results, Faculte Sciences, Marseille, France (1975).

99. P. Southwick and D. Sapper, J. Org. Chem., 19, 1926 (1954).

100. J. Okamiya, Nippon Kagaku Zasshi, 80, 783 (1959).

101. D. Suciu, Rev. Roumaine Chim., 18 677 (1973); Chem. Abstr., 79, 31324

102. M. P. V. Mijovic and J. Walker J. Chem. Soc., 3381, (1969).

103. L. M. Werbel, Chem. Ind. London., 39, 1634 (1966).

104. M. Selim, G. martin, and M. Selim, Bull. Soc. Chim. France, 8, 3268 (1968).

105. M. Selim, M. Selim and G. martin, Bull. Soc. Chim. France, 8, 3272 (1968).

106. R. Dahlbom, T. Ekstrand, S. Gronowitz, and B. Mathiasson, Acta Chem. Scand., 17, 2518 (1963).

107. J. P. Aune, R. Phan Tan Luu, E. J. Vincent, and J. Metzger, Bull. Soc. Chim. France, 7, 2679 (1972).

108. N. Fuson, M . L. Josien, J.Chem. Phys., 20, 145 (1952).

109. J. Kruegar and H. W. Thompson, Proc. Roy. Soc., A243, 143 (1957).

110. P. J. Kruegar, Nature, 194, 107 (1962). Can. J. Chem. 40, 2300 (1962).

111. A. R.Katriziky and P. S. Mons, J. Chem. Soc., 2051, 2058 (1959).

112. A. R. Katriziky and N. A. Coal's, J.Chem. Soc., 2062 (1959).

113. R. C. Paul and S. L. Chadha, J. Inorg. Nucl. Chem., 31, 2753 (1960).

114. M. Hall and G. B. B. M. Sutherland, Proc. Roy. Soc. (London). 236A (1956).

115. W. H. Koppenol and J. G. Traynham, Methods Enzymol., 268, 3 (1996).

116. R. G. Knowles and S. Moncada, Biochem. J., 298, 249 (1994).

117. L. J. Ignarro, R. E. Byrns, G. M. Buga, K. S. Wood, G. Chaudhuri, J. Pharmacol. Exp. Ther., 244, 181 (1988).

118. R. M. Palmer, D. S. Asthon, S. Moncada, Nature, 333, 664 (1988).

119. K. M. Miranda, M. G. Espey, D. Jourd'heuil, M. B. Grisham, J. M. Fucuto, M. Feelisch, D. A. Wink, in: L. J. Ignarro (Ed.), Nitric Oxide: Biology and Pathalogy, Academic Press, San Diego, 41, (2000).

120. F. Murad, Recent Prog. Harm. Res., 53, 43 (1998).

121. G. C. Brown, Biochim. Biophys. Acta, 1411, 351 (1999).

122. S. A. Lipton, Cell Death Differ., 6, 943 (1999).

123. M. M. Cals-Grierson and A. D. Ormerod, Nitric Oxide, 10, 179 (2004).

124. T. Andoh, C. C. Chiueh, and P. B. Chock, J. Biol. Chem.., 278, 885, (2003).

125. J. Benrath, M. Zimmermann, and F. Gillardon, Neurosci. Lett., 10, 17, (1995).

126. D. E. Heck, D. L. Laskin, C. R. Gardner, J. D. Laskin, J. Biol. Chem., 267, 21277 (1992).

127. Kazuhito Kawakita, Ayako Yamamoto, Shinpei Katou, Hirofumi Yoshioka, Noriyuki Doke, Nitric Oxide, 11, 37 (2004).

128. Victor Darley–Usmar, Nitric Oxide, 11, 40 (2004).

129. F. Y. Liew, F. E. Cox, Immunol. Today, 12, A17 (1991).

130. C. Blank, C. Bogdan, C. Bauer, K. Erb, H. Moll, Eur. J. Immunol., 26, 792 (1996).

131. K. D. Coren, J. Clin. Invest., 91, 2246 (1993).

132. R. Weller, S. Patullo, L. Smith, M. Golden, A. D. Ormerod, N. Benjamin, J. Invest. Dermatol., 107, 327 (1996).

133. R. Weller, R. J. Price, A. D. Ormerod, N. Benjamin, C. Leifert, J. Appl. Microbiol., 90, 648 (2001).

134. T. Schon, R. H. Hernandez-Pando, Y. Negesse, R. Leekassa, T. Sundiqvist, S. Britton, Br. J. Dermatol., 145, 809 (2001).

135. Y. J. Lim, S. E. Chang, J. H. Choi, K. J. Sung, J. H. Bahk, S. H. Do, D. S. Lee, J. Dermatol. Sci., 29, 201 (2002).

136. R. M. J. Palmer, M. J. Ferrige, S. Moncada, Nature, 327, 524 (1987).

137. S. Moncada, R. M. J. Palmer, and E. A. Higgs, Pharmacol. Rev., 43, 109 (1991).

138. T. G. Taylor and V. S. Sharma, Biochemistry., 31, 2847 (1992).

139. A. P. Hong, D. W. Bahnemann, M. R. J. Hoffmann, J. Phys. Chem., 91, 6245 (1987).

140. D. K. Lavellee, Coord. Chem. Rev. 61, 55 (1985).

141. M. Hoshino, L. Lavermann, and P. C. Ford, Coord. Chem. Rev. 187, 75 (1999).

142. I. J. Ostrich, G. Liu, H. W. Dodgen, and J. P. Hunt, Inorg. Chem. 19, 619 (1980).

143. T. W. Swaddle, A. E. Merbach, Inorg. Chem. 20, 4212 (1981).

144. Y. Zhao, C. Hoganson, G. T. Backcock, and M. A. Marletta, Biochemistry., 37, 12458 (1998).

145. A. M. Tyryshkin, S. A. Dikanov, E. J. Reijerse, C. Burgard, and J. Hutterman, J. Am. Chem. Soc., 121, 3396 (1999).

146. A. M. Rich, R. S. Armstrong, P. J. Ellis, and P. A. Lay, J. Am. Chem. Soc., 120, 10827 (1998).

147. S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A.. Ibers, and R. H. Holm, J. Am. Chem. Soc., 98, 2414 (1976).

148. C. Caron, A. Mitschler, G. Riviere, L. Ricard, M. Schapacher, and R. Wiess, J. Am. Chem. Soc., 101, 7401 (1979).

149. H. Ogoshi, H. Sugimoto, and Z. Yoshida, Tetrahedron Lett., 27, 2289 (1975).

150. T. Higuchi, S. Uzu, and M. Hirobe, J. Am. Chem. Soc., 112, 7051 (1990).

151. T. Higuchi, K. Shimada, N. Maruyama, and M. Hirobe, J. Am. Chem. Soc., 115, 7551 (1993).

152. T. Higuchi, and M. Hirobe, J. Mol. Catal. A, 113, 403 (1996).

153. N. Suzuki, T. Higuchi, Y. Urano, K. Kikuchi, T. Uchida, M. Mukai, T. Kitagawa, and N. Nagano, J. Am. Chem. Soc., 122, 12059 (2000).

154. H. Shoun, Y. Sudo, and T. Beppu, J. Biochem. (Tokyo), 94, 1219 (1983).

155. K. Nakahara, K. Tanimoto, K. Hatano, K. Usada, and H. Shoun, J. Biol. Chem., 268, 8350 (1993).

156. H. Shimizu, E. Obayashi, Y. Gomi, H. Arakawa, S. Y. Park, H. Nakamura, S. Adachi, H. Shoun and Y. Shiro, J. Biol. Chem., 275, 4816 (2000).

157. E. Obayashi, S. Takahashi, and Y. Shiro, J. Am. Chem. Soc., 120, 12964 (1998).

158. A. Daiber, T. Nauser, N. Takaya, T. Kudo, P. Weber, C. Hultschig, H. Shoun and V. Ullrich, J. Inorg. Biochem., 88, 343 (2002).

159. R. Silaghi-Dumitrescu, Eur. J. Inorg. Chem., 1048 (2003).

160. E. Obayashi, K. Tsukamoto, S. Adachi, S. Takahashi, M. Nomura, T. Iizuka, H. Shoun and Y. Shiro, J. Am. Chem. Soc., 119, 7807 (1997).

161. U. P. Singh, E. Obayashi, S. Takahashi, T. Iizuka, H. Shoun, and Y. Shiro, Biochim. Biophys. Acta, 103, 1384 (1998).

162. Y. Shiro M. Fujii, K. T. Iizuka, S. Adachi, K. Tsukamoto, K. Nakahara, H. Shoun, J. Biol. Chem., 270, 1617 (1995).

163. D. A. Scherlis, C. B. Cymeryng, and D. A. Estrin, Inorg. Chem. 39, 2352 (2000).

164. S. P. Singh, R. S. Mishra, S. S. Parmar and S. J. Brumleve, J. Pharm. Sci., 64 (7), 1245 (1978).

165. N. Siddiqui, S. N. Pandeya, G. S. Singh and A. P. Sen, Pharmkefitiki, 43, 121 (1992).

166. P. P. Desai and K. R. Desai, J. Indian Chem. Soc., 71, 153 (1994).

167. R. N. Ghaneim, M. Y. H. Essami, M. S. Mohmed and A. M. Kamal, Indian. J. Chem., 37B, 904 (1998).

168. U. Huseyin, K. Vanderpoorten, S. Cacciagaerra and S. Spampinto, J. Med. Chem., 41, 1138 (1998).

169. NORTHEY, Chem. Rev., 27, 85 (1940); Ind. Eng. Chem., 35, 829 (1943).

170. C. J. Sanderson, in: 'Biological and Environmental Aspects of chromium', ed. S. Langard, Elsevier, Amsterdam, p. 102

171. J. Krechel, T. Muller, and M. Augustin. Z. Chem. 281, 29 1989.

172. M. Nogueras, M.L. Quijano, A.Sanchez, and M. Melgarejo, Nucleosides Nucleotides 8, 117 (1989).

173. R.L. Lipnick and J.D. Fissekis, J. Org. Chem. 44, 4867 (1989).

174. T. Itoh, Y. Tomii, T. Naitoh, M. Yamamura, I. Ishikawa, N. Kawahara, Y. Mizuno, and H. Ogura, Chem. Pharm. Bull 37, 2197 (1989).

175. K. Hirota, H. Sajiki, Y. Kitade, and Y. Maki, Chem. Pharm. Bull. 37, 2008 (1989).

176. T. Itahara and N. Ide. Chem. Lett., 977 (1989).

177. M. Matsui, H. Nakazumi, K. Kamiya, C. Yatome, K. Shibata, and H. Muramatsu, Chem. Lett., 723 (1989).

178. H. Wamhoff and E. B. Walsh, Tetrahedron Lett. 29, 4401 (1989).

179. K. Hirota, Y. Kitade, K. Shimada, and Y. Maki, J. Org. Chem. 50, 1512 (1985).

180. G. L. Anderson, J. Heterocycl. Chem. 22, 1969 (1985).

181. P. A. J. Link, H. C. van der Plas, and F. Muller, J. Heterocycl. Chem. 22, 873 (1985).

182. P. A. J. Link, H. C. van der Plas, and F. Muller, J. Heterocycl. Chem. 22, 841 (1985).

183. N. Kawahara, T. Nakajima, T. Itoh, and H. Ogura, Chem, Pharm. Bull. 33, 4740(1985).

184. T. Nagamatsu, M. Ukai, F. Yoneda, and D. J. Brown, Chem. Pharm. bull. 33, 3113 (1985).

185. D. J. Brown, in "The Chemistry of Heterocyclic Compounds" (A. Weissberger and E. C. Taylor, eds.), Vol. 16, Suppl. 2, p. 248, 262ff. Wiley (Interscience), New York, 1985.

186. A. Ishida, S. Toki, and S. Takan aku, J.C.S. Chem. Commun., 1481 (1985).

187. H. Wamhoff, K. Wald, A. Kirfel, L. Farkas, N. Samimi, and G. Will, Chem. Ber. 118, 436 (1985).

188. H. Wamho, Adv. Heterocycl. Chem. 38, 229 (1985).

189. F. Lingens, H. Kraus, and S. Lingens, Hoppe–Seyler's Z. Physiol. Chem. 339, 1 (1984).

190. T. Harayama, Y. Tezuka, T. Taga, and F. Yoneda, Tetrahedron Lett. 36, 4015 (1984).

191. F. Yoneda, M. Koga, and T. Ibuka, Tetrahedron Lett. 25, 5345. (1984).

192. K. Tanaka, T. Okada, and F. Yoneda, Tetrahedron Lett. 25, 1741 (1984).

193. M. Arys, T.B. Christensen, and J. Eriksen, Tetrahedron Lett. 25, 1521 (1984).

194. K. Hirota, Y. Kitade, H. Sajiki, and Y. Maki, Synthesis 589 (1984).

195. T.-L. Su, K. Harada, and K. A. Watanabe, Nucleosides Nucleotides 3, 513 (1984).

196. H. O. Kalinowski, S. Berger, and S. Braun, "13C–NMR Spektroskopie." Thieme, Stuttgart, 1984.

197. D. J. Brown, in "Comprehensive Heterocyclic Chemistry" (A.R. Katritzky and C. W. Rees. eds.),Vol. 3, pp. 57, 142. Pergamon, Oxford, 1984.

198. T. L. Su and K. A. Watanabe, J. Heterocycl. Chem. 21, 1543 (1984).

199. H. Kanazawa, S. Nishigaki, and K. Senga, J. Heterocycl. Chem. 21. 969 (1984).

200. A.S. Prasad, J.S. Sandhu, and J. N. Baruah, J. Heterocycl. Chem. 21, 267 (1984).

201. K. Hirota, Y. Kitade, and S. Senda, J.C.S. Perkin 1, 1859 (1984).

202. K. Hirota, K. Maruhashi. N. Kitamura, T. Asao, and S. Senda, J.C.S. Perkin 1, 1719 (1984).

203. K. Hirota, t. Sugiyama, Y. Kitade, S. Senda, and Y. Maki, J. C. S. Perkin 1, 583 (1984).

204. T. Nagamatsu, Y. Hashiguchi, and F. Yoneda, J.C.S. Perkin 1, 561 (1984).

205. M. Sako, Y. Kojima, K. Hirota, and Y. Maki, Heterocycles 22, 2509 (1984).

206. K. Hirota, Y. Yamada, J. Haruta, and S. Senda, Heterocycles 22, 2309 (1984).

207. H. Wamhoff, A.Schmidt, and M. Nieger, TetrahedronLett. 32, 4473 1991.

208. P.Matyus, Neiger,and H. Wamhoff, PhosphorusSulfur, 63, 323 1991.

209. K.Hirota, H. Sajiki, P.-Z. Nitrosyl, Y.kitade,and Y.Maki, Tetrahedron 46, 3431 1990.

210. P. Molina andM. J. Vilaplana, Synthesis, 474 1990.

211. N. G. Kundu, B. Das, and M. Majumdar, Synthesis, 243 1990.

212. S. Broder, Med. Res. Rev. 10, 419 1990.

213. H. Wamhoff, H. Wintersohl, S. Stolben,J. Paasch, Zhu Naijue, and F. Guo, Liebigs Ann. Chem., 901 1990.

214. M. Matsui, K. Kamiya, K. Shibata, and H. Muramatsu,J. Org. Chem. 55, 1396 1990

215. K.Hirota, M. Shirahashi, S. Senda, and M. Yogo, J. Heterocycl. Chem. 27, 717 1990.

216. P. Bhuyan, R. C. Boruah, and J.S. Sandhu, J. Org. Chem. 55, 568 1990.

217. K. Hirota, Y. Kitada, H. Sajiki, and Y. Maki, J.C.S.Perkin 1, 367 1990.

218. T. Kimachi, M. Kawase, S. Matsuki, K. Tanaka, and F. Yoneda, J.C.S. Parkin 1 , 253 1990.

219. K. Hirota, ffH. Sajiki, Y. Kitade, and Y. Maki, J.C.S. Perkin 1 , 123 1990.

220. V. K. Ahluwalia, R. Tyagi, and M. Kaur, Indian J. Chem. , Sect.B 29B, 566 1990.

221. X. Chen, K. Tanaka, and F. Yoneda,Chem. Pharm. Bull. 38, 612 1990.

222. X. Chen, K. Tanaka, and F. Yoneda, Chem. Pharm. Bull. 38, 307 1990.

223. A. L. J. Beukwith and L. K. Dyall, Aust. J.Chem. 43, 451 1990.

224. L. F. Tietze, S. Brand, T. Brumby, and J. Fennen, Angew. Chem., Int. Ed. Engl. 29, 665 1990.

225. L. F. Tietze, S. Brand, T. Brumby, and J. Fennen. Angew. Chem. 102, 675 1990.

226. M. Alam and N. Siddiqui, Indian. J. of Heterocyclic Chem., 13, 361(2).